UNIVERSITY OF EDINBURGH.

IONIC INTERCHANGE

and

STABILITY IN COLLOIDAL SYSTEMS.

by

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Thesis presented for the
degree of
Doctor of Philosophy.

October 1938.

CONTENTS.

INTRODUCTION.

The mechanism of the coagulation of aqueous colloidal dispersions of inorganic substances by electrolytes is still an open question despite numerous investigations since the pioneer observations of Schulze.[1] While it is generally agreed that the stability of such systems depends upon the presence of electrical charges on the surface of the particles, there is divergence of opinion with regard to the way in which the stabilising influence of these charges is nullified by the presence of the coagulant. In particular it has not yet been found possible to account in a satisfactory manner for the differences in the coagulative power of the various electrolytes.

An early view, at one time strongly advocated by Freundlich,[2] postulated that the oppositely charged ions of the coagulating electrolyte united with the stabilising ions on the surface of the particle to give electrically neutral complexes, thereby reducing the charge to zero, or at least to such an extent that the electrical repulsion between the particles was no longer sufficient to keep them apart. The nature/

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1. Schulze, J. pr. Ch., 25 (1882) 431; 27 (1883) 320.
2. Freundlich, Koll. Zeitchr., 1 (1910) 321.

nature of the union between stabilising and coagulating ions was not specified, beyond that the coagulating ions were said to be "adsorbed" by the particles. It is evident that, according to this hypothesis, for a given quantity of a given sol, electrically equivalent amounts of all coagulating ions will be adsorbed at the respective coagulating concentrations, provided no other type of adsorption occurs.

Freundlich, Weiser, and others ① determined directly the adsorption of the oppositely charged ions at or above the coagulation point in a large number of cases, but the results provided little evidence of the existence of the effect in question. That the failure to observe equivalence might be due to the occurance of some other type of adsorption was eventually demonstrated by Weiser ②, who showed that the adsorption could continue to increase to electrolyte concentrations far above those sufficient to produce complete coagulation.

It/

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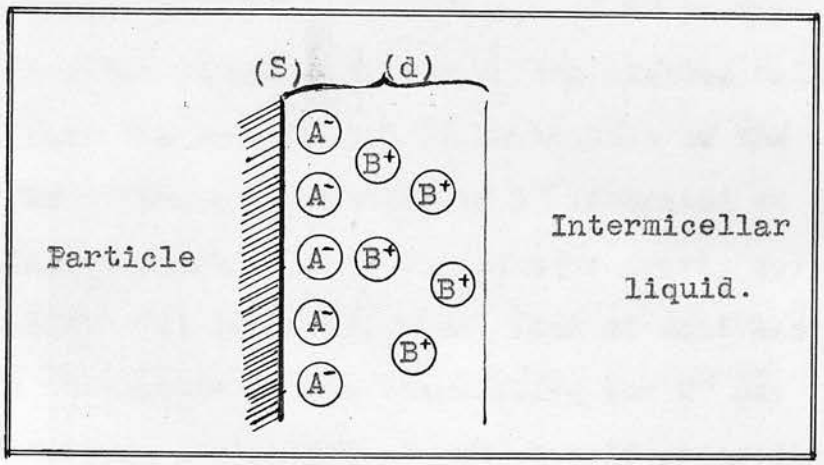
① Freundlich, Joachimsohn & Ettisch, Z. phys. Chem., 141(1929) 249; Freundlich, Kapillarchemie, II (1932) 130, 131; Whitney & Ober, J.A.C.S., 23 (1902) 842; Weiser, J.Phys. Ch. 25 (1921) 399; 29 (1925) 955; Alexander's "Colloid Chemistry", I (1926) 602 et seq. Weiser & Middleton, J. Phys. Ch. 24 (1920) 30, 630.

② Weiser, J. Phys. Ch., 25 (1921) 399; 29 (1925) 955. Weiser & Milligan, J. Phys. Chem. 40 (1936) 1071

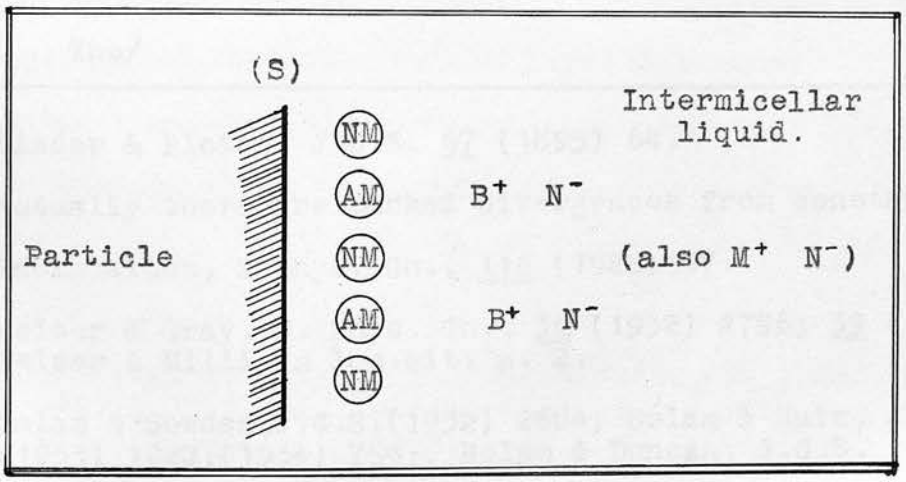
It would, however, appear possible to discrimin-:ate experimentally between the type of adsorption postulated by Freundlich and other accompanying adsorption processes. If, for example, the stabilising ions on the surface of the particle are negatively charged, they will hold in their neighbourhood, close to the particle, an electrically equivalent amount of some positive ion. An electrical double layer is thus formed as represented in the following diagram:-



where (A⁻) represents the stabilising ions (either adsorbed on the surface (S) or originating from ionisation of the surface molecules themselves) and (B⁺) the compensating⊛ positive ions forming the outer part of the double layer. The positive ions are mobile but have a range of movement (d) away from the surface limited by the electrostatic attraction of the inner fixed negative layer. It is evident that if a salt MN be introduced into the sol, interchange will/

⊛ frequently termed "counter ions"

will take place between the ions M^+ and B^+ so that a proportion of the latter, depending upon the concen-:tration, will be liberated from the neighbourhood of the surface and appear in the body of the inter-:micellar liquid. If combination occurs between A^- and M^+ to form electrically neutral complexes, the interchange will be complete when the whole of A^- is so combined. Thus if complete, or almost complete, neutralisation of the charge is the condition for coagulation, the concentration of B^+ in the intermicellar liquid will attain its maximum value at or near the coagulating concentration of the salt MN. Hence the amount of B^+ liberated at the coagulation point will be the same (or nearly so) for all salts. It is obvious that lack of equivalence in the adsorption of the coagulating ion M^+ may arise through adsorption of MN itself proceeding alongside the taking up of M^+ by interchange with B^+, as represented in the following diagram:



There/

There is no reason to suppose that such adsorption of the "total salt" will have the same value for all electrolytes at the coagulation point.

Freundlich, Joachimsohn, and Ettisch (loc. cit. p. 2) actually record measurements of the replacement of hydrogen ion from the micelles of arsenious sulph-:ide sols (previously observed by Linder & Picton ① and Whitney and Ober - loc. cit. p. 2), but though remarking that the amounts liberated by various salts at their respective coagulation values are very similar ②, these workers overlooked the possible significance of the phenomenon. The study of ionic interchange in systems where the hydrogen ion is the counter ion has, however, been taken up by a number of other investigators, notably Rabinowitch ③ (arsenious sulphide sol), Weiser ④ (arsenious sulphide, sulphur, and copper ferrocyanide sols), Bolam ⑤ (sulphur and stearic acid sols), and Verwey ⑥ (silver iodide sols).

The/

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① Linder & Picton, J.C.S. 67 (1895) 64.

② Actually there are marked divergences from constancy.

③ Rabinowitch, Z.phys. Ch., 116 (1925) 97.

④ Weiser & Gray, J. Phys. Ch., 36 (1932) 2796; 39 (1935) 1163.
Weiser & Milligan loc.cit. p. 2.

⑤ Bolam & Bowden, J.C.S. (1932) 2684; Bolam & Muir, J.C.S. (1933) 1022; (1934) 754; Bolam & Duncan, J.C.S. (1936) 1317.

⑥ Verwey & Kruyt, Z. phys. Ch. 167A (1934) 312;
Verwey, Chem. Reviews, 16 (1935) 363.

The results of these investigations show that (1) for for a given sol the order of the replacing powers in a series of salts is invariably the same as the order of their coagulating powers, and (2) frequently the replacement of hydrogen ion arrives at its maximum value in the region of the coagulation point.. Thus there appears to be considerable justification for the view that the process of ionic interchange is of significance for the elucidation of the mechanism of coagulation.

Weiser ① postulates that the stability of a sol depends upon the value of the (hypothetical) electro-:kinetic potential across the double layer, which is assumed to be directly proportional to the thickness (d) of the double layer. Coagulation is ascribed to the replacement of the original counter ions of the sol by the kations (if the sol is negative) of the added salt, which owing to their nature and concen-:tration approach more closely to the surface of the particle, so that the double layer undergoes contraction and the electrokinetic potential is decreased. Thus the actual charge on the particle is/

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① see references on page 5. Also Weiser, J. Phys. Ch., 35 (1931) 1, 1368; Weiser, Milligan, and Coppoc, J. Phys. Chem., 42 (1938) 427.

is not neutralised as in Freundlich's theory.

Weiser considers that his hypothesis (1) does not require that the degree of interchange at the coagulation point should be the same for all electro-:lytes, and (2) requires that the coagulation value should not be greater than the concentration of electrolyte which is sufficient to produce the maximum of interchange. He regards his data as indicating that these conditions are fulfilled, and that the ionic interchange is of primary importance.

Verwey and Kruyt (1), on the other hand, take the view that while adsorption in the sense of Freundlich's hypothesis is, under certain circumstances, respons-:ible for the coagulation, in general, decrease in stability is due to contraction of the double layer. This effect is regarded as a direct consequence of the increase in the bulk concentration of the coagulating electrolyte, whereas Weiser attributes the contraction specifically to the action of those ions which take the place of the original counter ions. Thus Verwey and Kruyt maintain that in most cases/

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(1) See references on page 5. Also "Symposium on the Dynamics of Hydrophobic Suspensions and Emulsions" (1937), reprinted from Chem. Weehblad (1938) p.p. 11 - 13, 71 - 78.

cases the ionic interchange does not play a signif-:icant part in the coagulation, but is a quite incidental process. They consider that their arguments are supported by experiments in which the interchange appears to be complete at a concen-:tration far below the coagulation value.

The object of the present investigation was to amplify the work of Bolam and co-workers ① on ionic interchange in sulphur and stearic acid sols. The data obtained by these workers indicate (1) that the interchange is complete at or above the coagulating concentration and (2) that the degree of interchange at the coagulation point is the same for all electro-:lytes. It is obvious that these results are not consonant with the views of Weiser, Verwey and Kruyt.

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① See references on page 5.

E X P E R I M E N T A L.

Preparation of (Raffo) Sulphur Sol

Colloidal sulphur was prepared by decomposing sodium thiosulphate with concentrated sulphuric acid. Both these reagents, and also the sodium chloride and hydrochloric acid used in the later stages of the preparation, were of A.R. or 'Analar' quality.

Only a small quantity of colloid can be prepared in one operation since the use of large quantities of thiosulphate and sulphuric acid results in the formation of a sulphur precipitate which will not peptise on warming with water. The following procedure was therefore carried out and repeated until a sufficient quantity of sol had been prepared.

25 ml. concentrated sulphuric acid were slowly run into 100ml. saturated aqueous solution of sodium thiosulphate, the mixture being vigorously stirred mechanically, and the temperature kept below 30°C. By surrounding the reaction vessel with a freezing mixture. Immediately the addition was complete, the mixture was cooled to 0°C., and 100 ml. saturated aqueous solution of sodium chloride was added. The coagulated sulphur was now filtered off in a Buchner funnel, and re-peptised by heating to 80°C./

80° C: in 100 ml. distilled water.

Coagulation and peptisation were repeated until all excess sulphuric acid was removed, i.e. until the supernatent liquid was neutral to litmus. Four coagulations were generally sufficient for this purpose. After the final dispersion in water, all the coarse sulphur was removed by centrifuging at 9,000 revolutions per minute for 15 minutes. A perfectly clear sol was obtained in this way.

When several small quantities of sol had been prepared as described, they were mixed together, cooled in ice, and coagulated with concentrated hydrochloric acid. The coagulum was filtered off as before, using toughened paper to withstand the concentrated acid, and redispersed by warming with water. This last stage was repeated again, the coagulum being sucked as free as possible from acid by the filter pump. The coagulum, now freed from sodium chloride, was re-dispersed in water, and the resulting sol stored in a Jena glass bottle and protected from the action of daylight. No attempt was made to remove the intermicellar hydrochloric acid by dialysis. A very stable, polydisperse, sol was/

was obtained.

Volume Measurements.

As will be appreciated from the foregoing description, it was undesirable to use a large volume of sol for an individual experiment. In making mixtures of sol and salt, therefore, 2 ml. only of sol were used in most cases. Since equal volumes of sol and salt solution were required for all determin: :ations, the same pipette was used for measuring both quantities. In certain cases, when only a "nephelo- :metric value" was required, it was possible to use 1 ml. sol and 1 ml. salt. The pipettes used - two of 2 ml capacity and one of 1 ml. capacity - were calibrated and found to give a sufficiently constant delivery as will be seen fron Table I

Table I

1 ml. Pipette.		
Weight of water delivered.	Mean Weight.	Divergence from mean.
1.0142 gms.		- 0.0002 gms.
1.0133 "		- 0.0011 "
1.0126 "	1.0144 gms.	- 0.0018 "
1.0131 "		- 0.0013 "
1.0190 "		+ 0.0046 "
Maximum error ± 0.0046 gm. i.e. 0.5%		
(Temperature = 18° C.)		

2 ml. Pipettes./

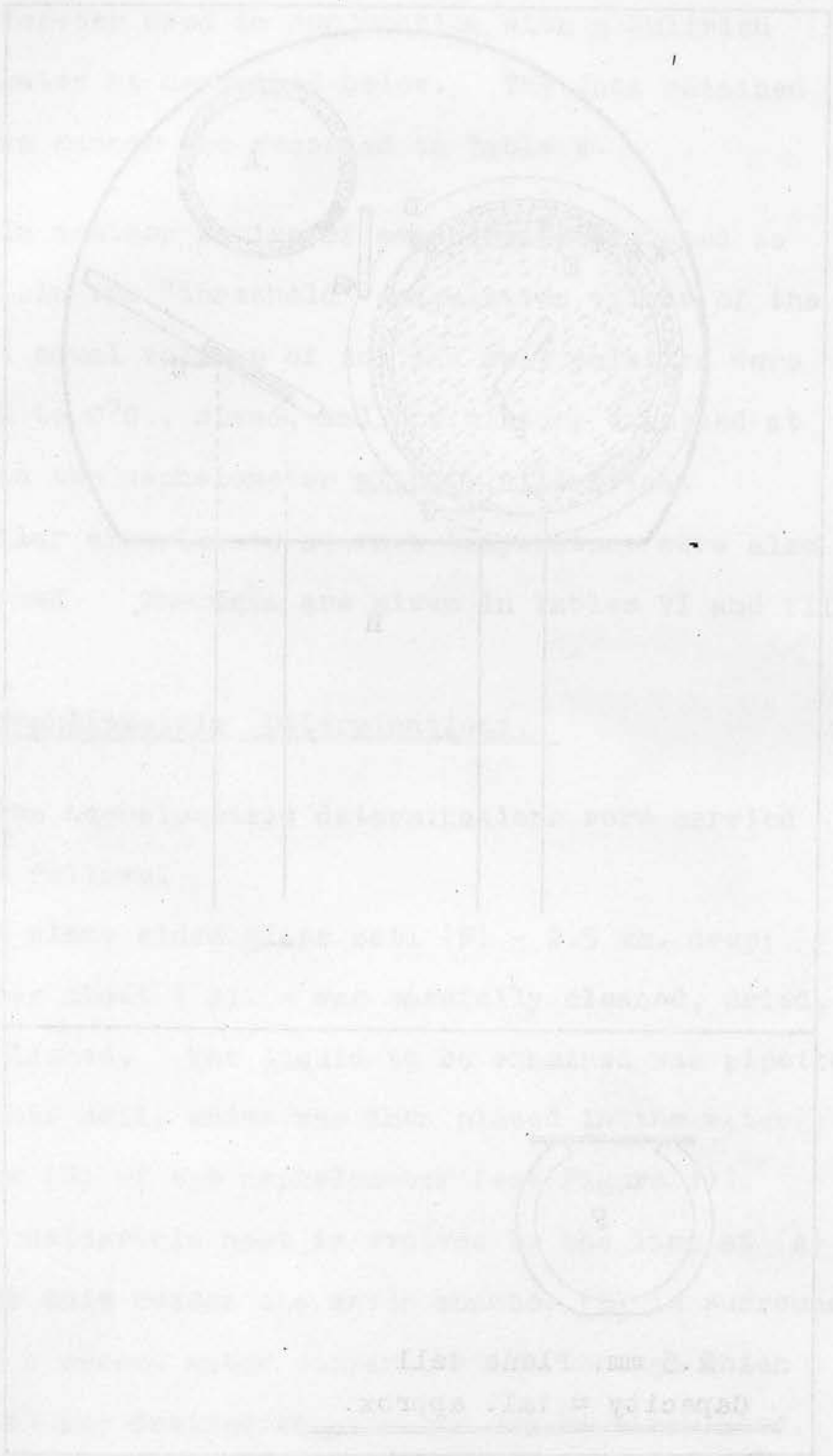
Table I (continued)

2 ml. Pipette (A)		
Weight of water delivered (grams)	Mean weight.	Divergence from mean (grams)
1.9901		- 0.0064
1.9795		- 0.0170
2.0028	1.9965gm.	+ 0.0063
2.0077		+ 0.0112
2.0023		+ 0.0058
Maximum error ± 0.0170 gm. i.e. 0.8% (Temp. 18°C.)		
2 ml. Pipette (B)		
1.9850		+ 0.0014
1.9854		+ 0.0018
1.9832	1.9836gm.	- 0.0004
1.9843		+ 0.0007
1.9801		- 0.0035
Maximum error ± 0.0018 gm. i.e. 0.09% (Temp. 18°C.)		

Coagulation Experiments.

In one series of experiments, covering almost the whole range of coagulation, equal volumes of sol and salt solution were mixed at room temperature and any coagulated sulphur removed by filtration through a Jena 'sintered' glass filter of the finest porosity (5/3).⊛ The degree of coagulation was determined by measurement of the intensity of the light scattered by the uncoagulated sulphur in the filtrate./

⊛ That none of the sulphur in the uncoagulated sol was retained by the filter is shown by the data in Table VIII - page 37.



PLAN VIEW OF NEPHELOMETER.

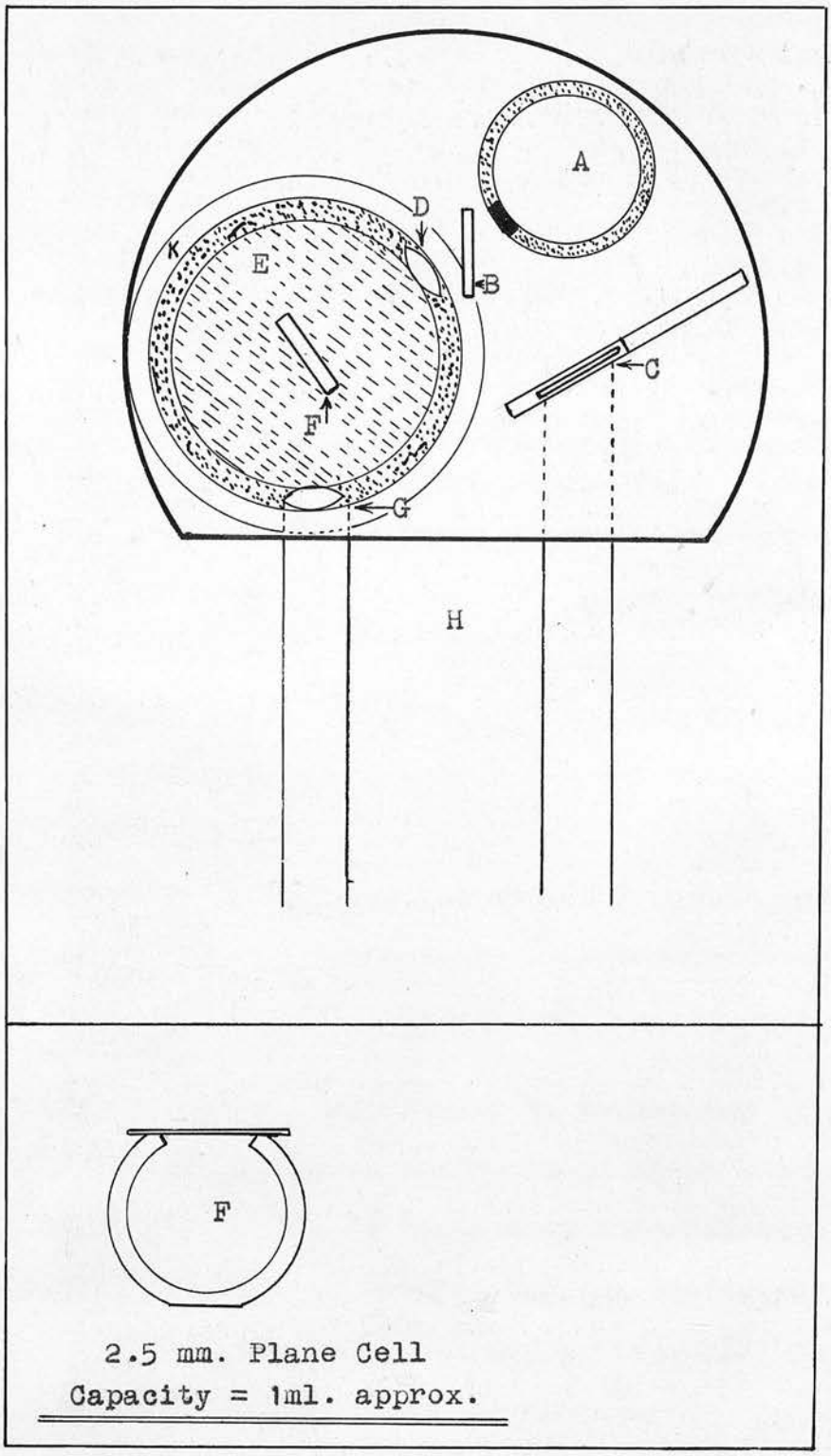


Figure 1.

filtrate. This was achieved by means of a Zeiss nephelometer used in conjunction with a Pulfrich photometer as described below. The data obtained in this manner are recorded in Table V.

In another series of experiments designed to ascertain the "threshold" coagulation values of the salts, equal volumes of sol and salt solution were cooled to 0°C., mixed, and the mixture examined at 0°C. in the nephelometer without filtration.

Similar experiments at room temperature were also performed. The data are given in Tables VI and VII.

Nephelometric Determinations.

The nephelometric determinations were carried out as follows.

A plane sided glass cell (F) - 2.5 mm. deep; capacity about 1 ml. - was carefully cleaned, dried, and polished, The liquid to be examined was pipetted into this cell, which was then placed in the water chamber (E) of the nephelometer (see Figure 1).

Considerable heat is evolved by the lamp at (A), and for this reason the water chamber (E) is surrounded by a second water compartment(K) through which water at any desired temperature may be circulated.

In the second series of experiments ice-cold water was circulated through (K) in order to maintain (E) and/

and (F) at $0^{\circ}C$.

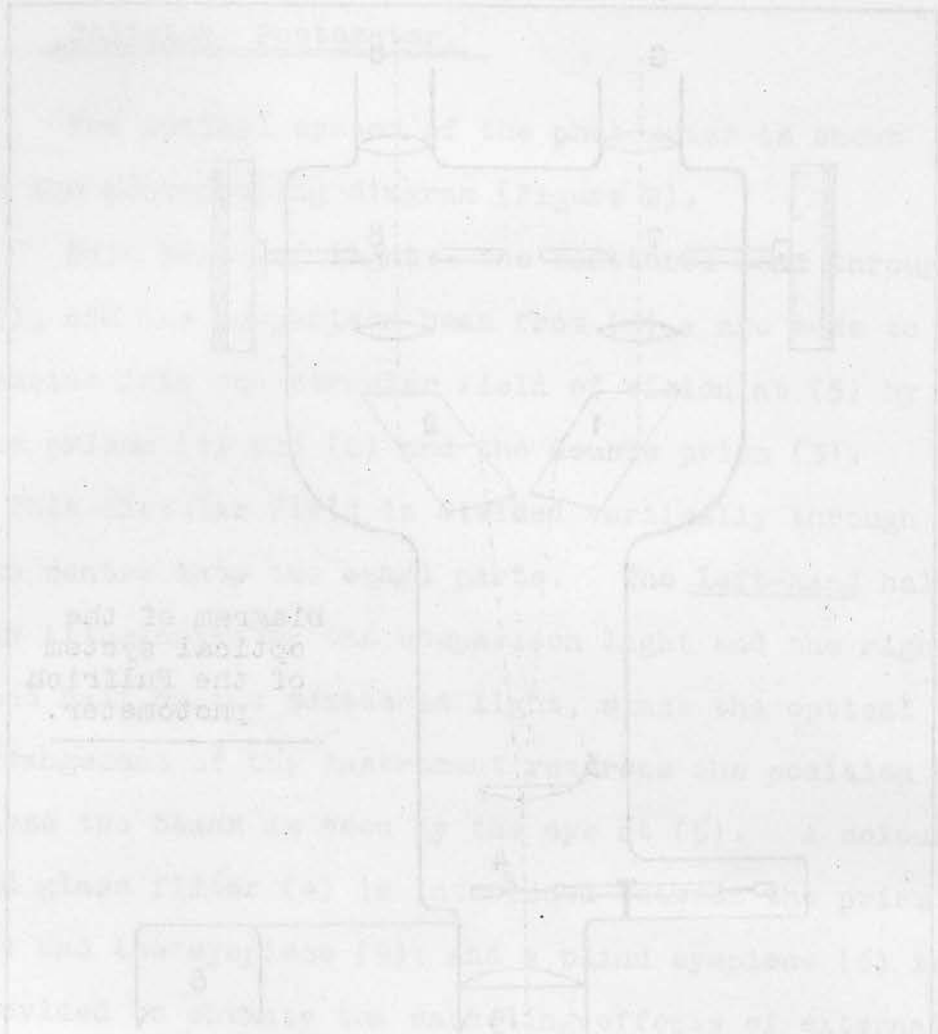
Light from a 30 watt filament lamp (A) is split into two beams by striking a glass plate (B), placed (as shown) at an angle. The light reflected from this plate now passes through a ground glass screen (C) and this beam constitutes the "comparison light".

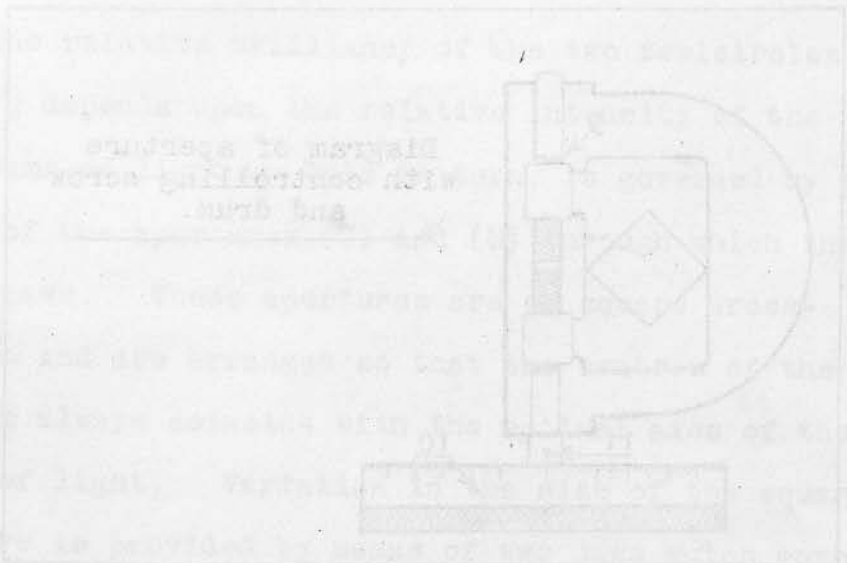
Light from (A) which is transmitted by (B) is focussed by the lens (D) into a ray of uniform (square) cross section. The cell (F) is held in position as shown, so that it is exactly at right angles to this square beam. Particles of solid present in (F) cause scattering of this beam. The scattered light is focussed by a lens (G) and the intensities of the two beams - one from (C) and one from(G) - are compared by means of the Pulfrich photometer.

It was found advisable to filter the water used for filling (E) since the presence of dust particles caused scattering of the light, and gave a false (high) reading of the intensity of the beam emerging at (G).

Any one of four ground glass screens may be placed in position at (C) to give a comparison beam of a suitable intensity. Screen No.4, giving the brightest comparison beam, was used throughout the work on the sulphur sol.

Pulfrich/





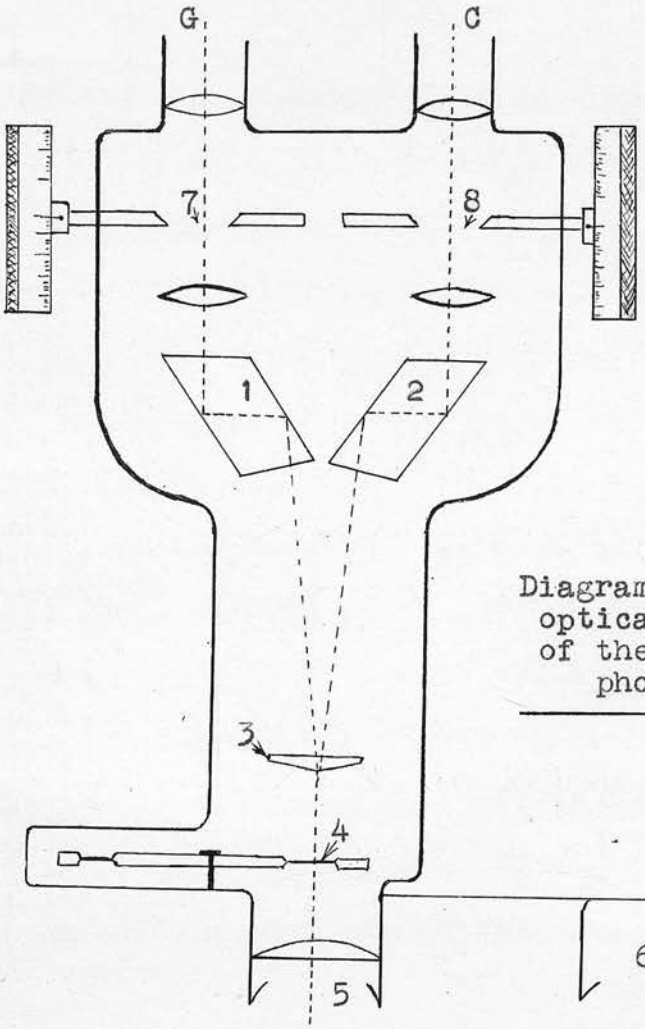


Diagram of the optical system of the Pulfrich photometer.

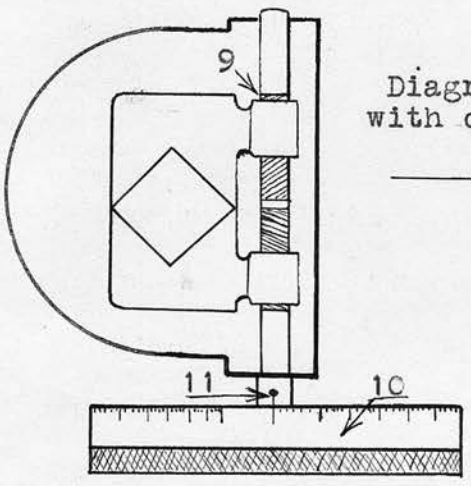
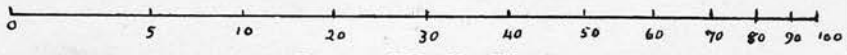


Diagram of aperture with controlling screw and drum.



Drum-scale rolled flat.

Figure 2

Pulfrich Photometer.

The optical system of the photometer is shown in the accompanying diagram (Figure 2).

Both beams of light - the scattered beam through (G), and the comparison beam from (C) - are made to combine into one circular field of vision at (5) by the prisms (1) and (2) and the double prism (3).

This circular field is divided vertically through the centre into two equal parts. The left-hand half is illuminated by the comparison light and the right-hand half by the scattered light, since the optical arrangement of the instrument reverses the position of these two beams as seen by the eye at (5). A colour-:ed glass filter (4) is interposed between the prism (3) and the eyepiece (5); and a blind eyepiece (6) is provided to obviate the dazzeling effects of external light.

The relative brilliancy of the two semicircles at (5), depends upon the relative intensity of the two beams of light. This in turn, is governed by the sizes of the apertures (7) and (8) through which the beams pass. These apertures are of square cross-section and are arranged so that the centres of the squares always coincide with the optical axes of the beams of light. Variation in the size of the square aperture is provided by means of two jaws which move in the same plane in opposite directions, each provided with/

with a 'V' shaped slot (see inset diagram - Fig.2).

Simultaenous movement of the two jaws in the direction of one of the diagonals of the aperture is obtained by means of a micrometer screw (9) which may be rotated by turning the drum (10). When the jaws are in the position shown in the diagram, the aperture is at maximum size, and therefore the intensity of the beam passing through it will also be at a maximum. By bringing the jaws closer to one another, the aperture size (and the light beam intensity) is reduced.

A scale is marked upon the periphery of the drum (10) so that its position relative to a line (11) on the body of the instrument may be ascertained. This scale is arranged so that when the drum reading is zero, the aperture is closed, while a reading of 100 represents the aperture fully open. Divisions on the scale, however, are not equal, the distance between '0' and '25' occupying about half of the drum periphery, while the increasingly smaller divisions between '25' and '100' occupy an approximately equal space (see diagram - Figure 2).

In using the Photometer, one drum is set at '100', while the other is adjusted until the two halves of the field of vision are of equal brilliancy.

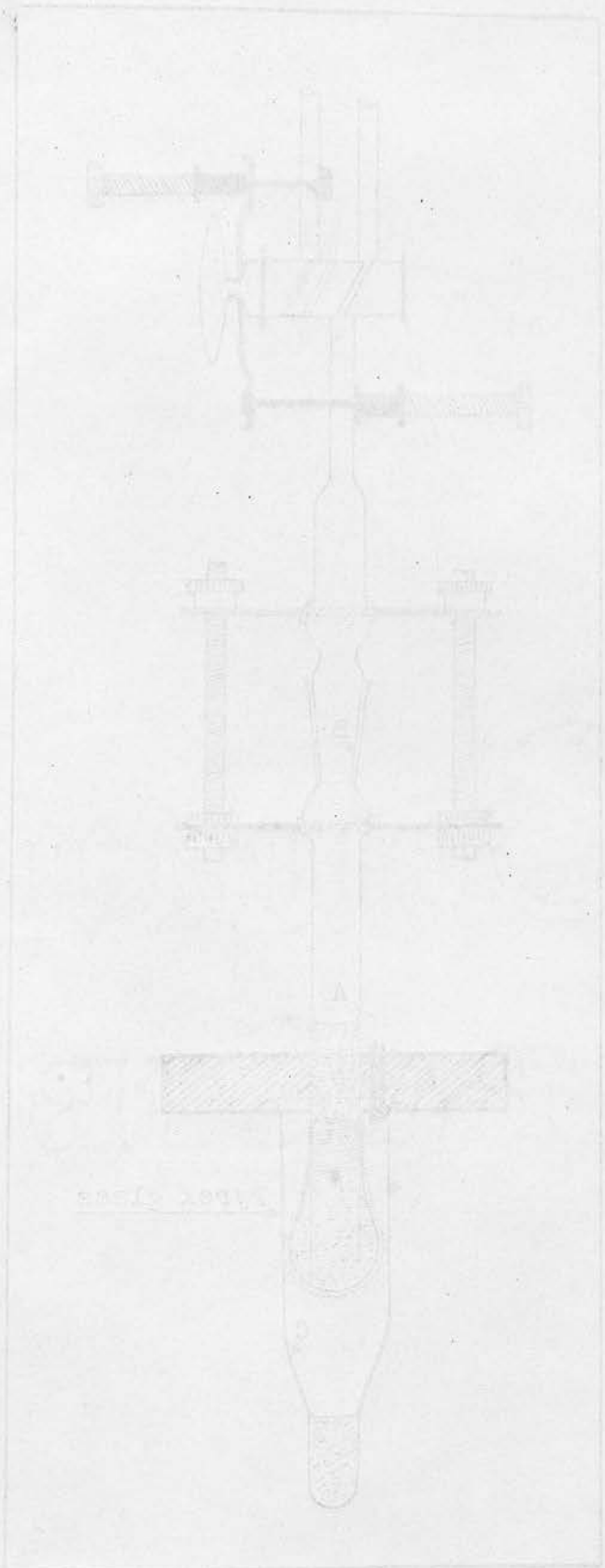
If this adjustment is carried out by turning the right/

right-hand drum so as to reduce the intensity of the comparison light, the drum reading now gives a measure of the intensity of the light scattered by the liquid in (F) directly. We may call this reading the "Nephelometric Value". Adjustment by means of the left-hand drum (with the right-hand drum set at '100') gives a reading 'X' which bears the following relation to the "Nephelometric value" of the liquid in (F):-

$$\text{"Nephelometric Value"} = 100 \times \frac{100}{\text{'X'}}$$

Five drum readings were taken with any one 'test' liquid, and the mean reading gave the "Nephelometric value" either directly or by use of the formula as explained above. Any value greater than that obtained with pure water, indicated the presence of solid particles of a colloid and/or a coarse suspension in the 'test' liquid in (F).

Figures obtained for the "Nephelometric value" depend upon,(1) the comparison screen (C) employed in the nephelometer, and (2) the colour of the glass filter (4) used in the Photometer. Alteration of either of these two factors will give a different reading with any one 'test' liquid. The No.4 ground-glass comparison screen, and a light green filter (No.L_2) were used throughout the sulphur sol investig: :ation



ULTRAFILTRATION APPARATUS

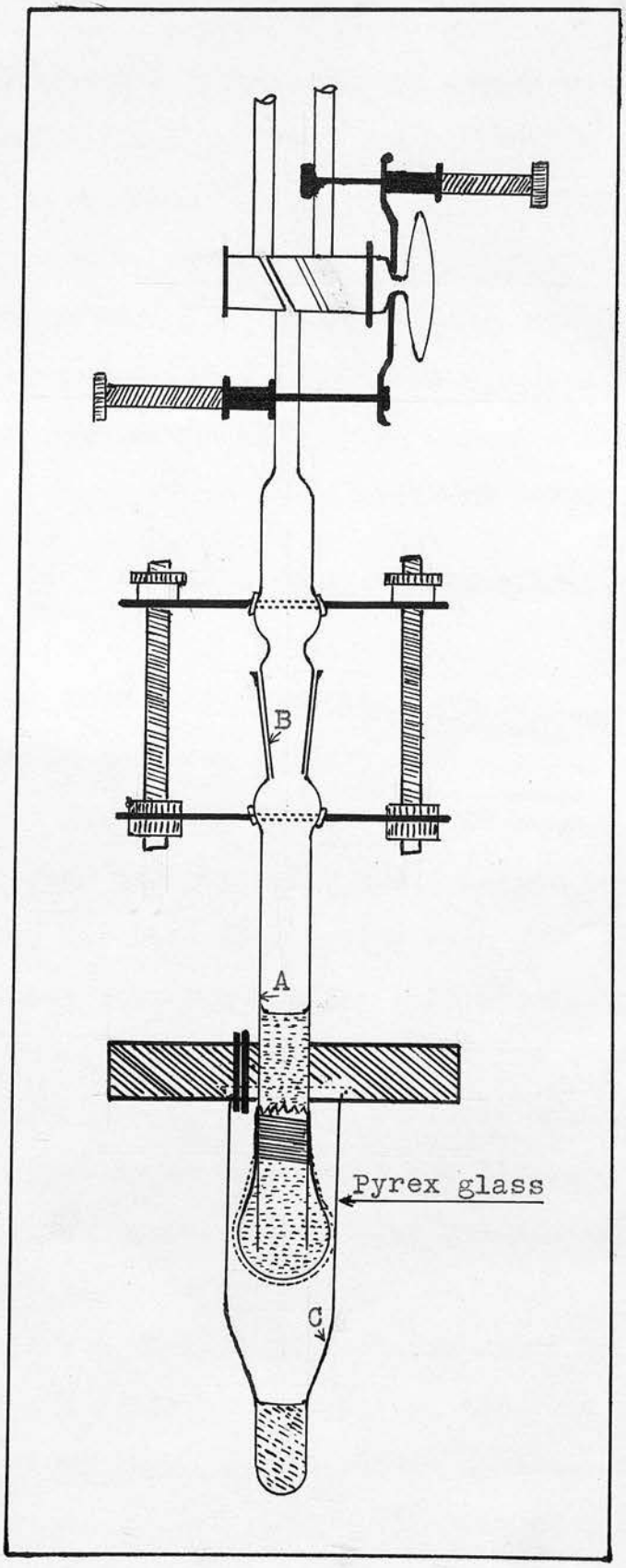


Figure 3.

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Ultrafiltration.

In order to determine the amount of hydrogen ion liberated from the micelles by interchange with the kations of an added salt, it was necessary to remove both coagulated and colloidal sulphur from the mixture. The filtration apparatus is described in detail by Bolam and Bowden (loc. cit. p. 5).

Cellophane (plain colourless No. 300) supplied by the Cellophane Company Ltd. was used as the filtration membrane. A piece of this material about 3" square, was carefully and tightly bound over the end of a glass tube (A) - about 1 cm. diameter - with linen thread (see Figure 3). A thimble of welded platinum gauze was now slipped over the cellophane and bound to the glass tube (A) in the same way. This served to support the cellophane when it became distended under pressure (about two atmospheres).

The liquid mixture to be ultrafiltered was introduced into tube (A) by pipette and the tube was then attached to the rest of the apparatus by the ground glass joint (B) as shown. All taps were held in position and joints held together by brass strips and screw clips to withstand the pressure.

Filtration was very slow, about 3 - 4 hours being required to obtain 2 ml. ultrafiltrate. Under these conditions/

conditions it was necessary either to eliminate evaporation or to determine the necessary correction.

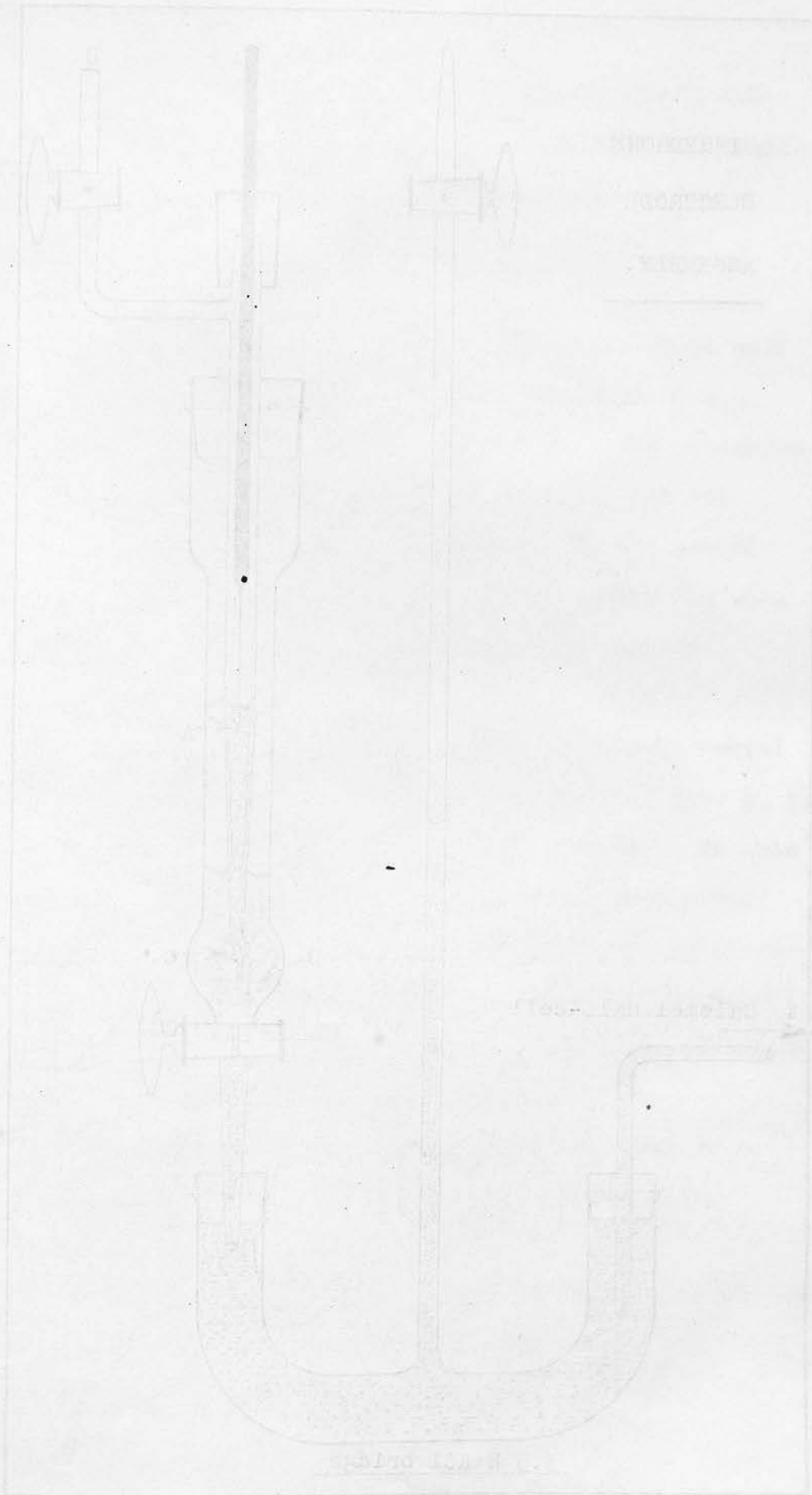
An improved type of ultrafiltrate receiver (C) was employed (see Figure 3) which was practically a closed vessel. According to Bolam and Muir (loc. cit. p. 5) the evaporation correction factor with this type of receiver is zero, and no correction was therefore made. When ultrafiltration of mixtures at 0°C. was required, the receiver was completely surrounded by crushed ice contained in a 'thermos' flask. Reference to Figure 3 will show that the liquid both before and after its passage through the cellophane membrane was thus practically all in an atmosphere maintained at 0°C. Evaporation, negligable even at room temperature, will, of course, be still less at 0°C.

Determination of Ionic Interchange.

Increase in the hydrogen ion concentration in the intermicellar liquid due to ionic interchange was determined by means of the quinhydrone electrode. ①

Since it was not dialysed, the sulphur sol contained a considerable quantity of hydrochloric acid in the intermicellar liquid. Hence it was necessary to reduce the concentration by adding to the ultrafiltrate/

① Biilmann. Annales de Chemie. 15 (1921), 128.



QUINHYDRONE

ELECTRODE

ASSEMBLY.

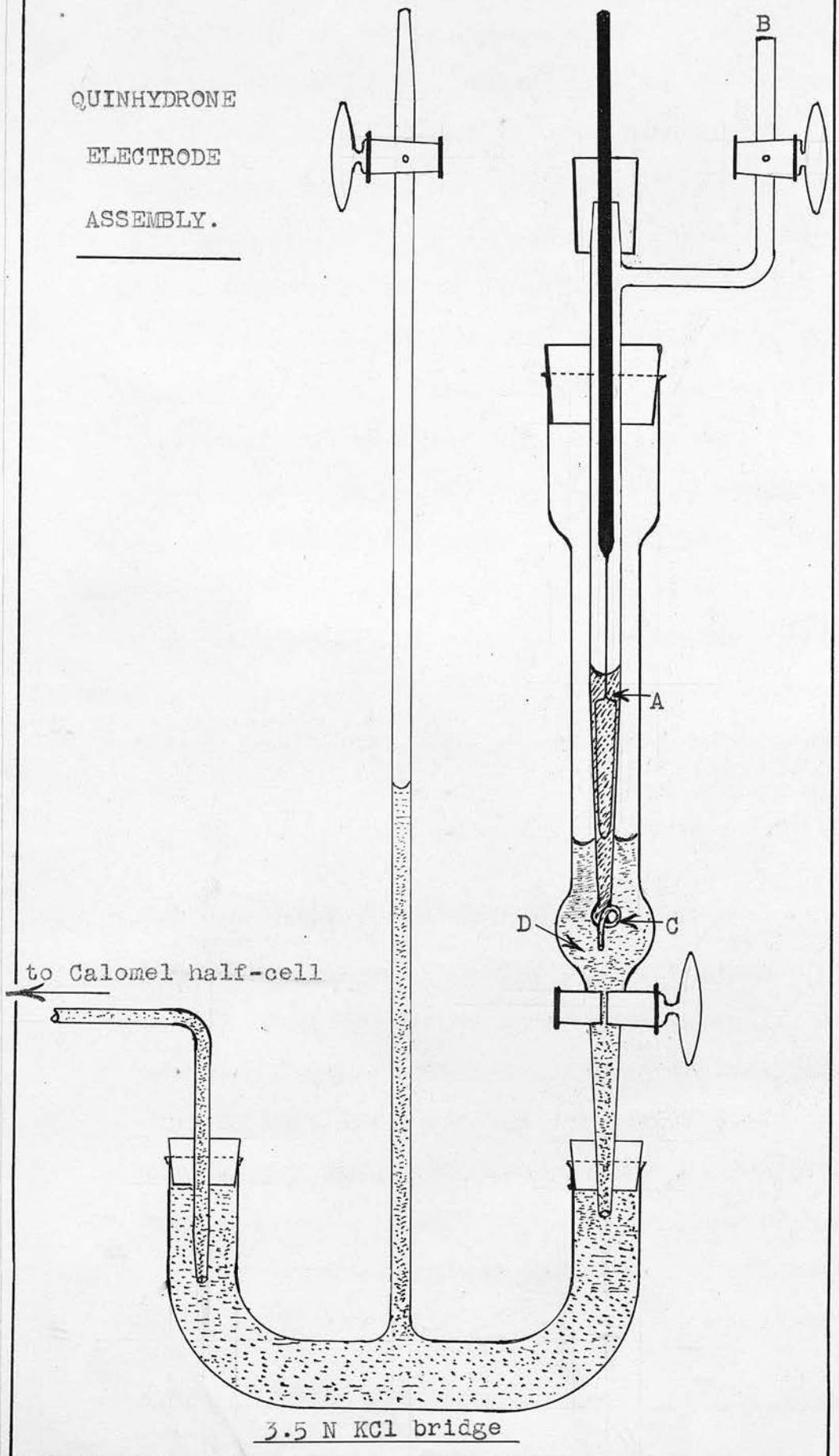


Figure 4.

ultrafiltrate a known volume of a dilute alkali sol-:ution (0.00627 N. NaOH), and then estimate the remain-:ing acid with the quinhydrone electrode.

Quinhydrone was prepared by the method of Biilmann and Lund.①

A 3.5 N. calomel electrode formed the other half of the cell, connection being made by means of a 3.5 N.KCl bridge as shown in Figure 4. The potassium chloride employed was of 'Analar'quality, and the calomel was prepared electrolytically by the method due to Lipscomb & Hulett② from mercury which had been twice washed in nitric acid, dried, and finally distilled in vacuo.

The special type of quinhydrone electrode vessel shown was designed by Bolam and Bowden (loc. cit. p. 5) for use with small volumes of 'test' liquid. In this investigation the cell was reconstructed from Pyrex glass. The 'test' solution (from 1 - 2 ml. sufficed) was drawn into the tube (A) by applying suction at (B). The complete turn at (C) served to cut down diffusion into the KCl solution to a minimum.

The ordinary Poggendorff circuit was used in conjunction with a high sensitivity, moving coil, mirror/

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① Biilmann & Lund. Ann. de Chemie 16 (1921), 339.

② Lipscomb & Hulett. J.Amer. Chem.Soc. 38 (1916), 21.

mirror galvanometer by Gambrell Bros., and a Tinsley 'Ionisation' potentiometer which could be read to 0.1 millivolts. Tinsley also supplied the standard Weston cell (N. P. L. calibration).

Hg	HgCl (solid)	KCl 3.5N	KCl 3.5 N bridge	'test' soln.	Quinhydrone solid	Pt. foil (polished)

The complete cell, which is shown diagramatically above, was set up in an electrically controlled air thermostat maintained at 25° C.(± 0.2° C.), the calomel half-cell being kept permanently in this thermostat.

Solid quinhydrone was added to the 'test' solution contained in a small Pyrex, stoppered tube of about 7 ml. capacity. This mixture was vigorously shaken, and then placed in the air thermostat where it was allowed to remain for at least 10 minutes.

Shaking was repeated frequently during this time to hasten the process of saturation of the liquid with quinhydrone, and also to make certain that the solution temperature was uniform. After the cell had been carefully washed with distilled water, it was rinsed out with the 'test' solution and filled. To avoid as far as possible, any cooling of the 'test' solution below 25° C. its transfer to the cell was carried/

carried out rapidly. The platinum foil was washed in distilled water and dried by heating in an alcohol flame before inserting it into the cell, while the KCl solution in (D) -Fig. 3 - was renewed before each E. M. F. determination.

E;M.F. readingsgiven in the subsequent tables were taken immediately after the cell had been filled and assembled. A slight falling off in the E.M.F. was observed after the cell had been allowed to stand for 15 minutes, - a third reading taken 30 minutes after assembly was practically identical with that taken after 15 minutes. Duplicate exper-:iments, however, showed that initial readings were quite reproducable. A maximum error of 0.2 milli-:volts was involved in the determination of the null point.

Calibration of the Quinhydrone Electrode.

Calibration of t he electrode was carried out by using mixtures of hydrochloric acid and sodium hydroxide of known composition.

In the first series of measurements 2 ml. of hydrochloric acid (0.01498 N.) and a known volume of sodium hydroxide (0.00627 N.) only, were used.

Table III shows the results obtained with these mixtures/

mixtures. A second series of experiments was carried out with mixtures made up as follows: 2 ml. HCl (0.01498 N.) were mixed with a known volume of NaOH (0.00627 N.), and then a volume, equal to that of the mixture, of water or of a salt solution was added. Results obtained with these mixtures containing water or salt solution are given in Table IV.

All the above mixtures were made up in pyrex stoppered tubes. 2 ml. hydrochloric acid was measured by means of a calibrated pipette (see p. 12), and the sodium hydroxide and salt solutions were added from a small (5 ml.) burette. This burette was calibrated by weighing the volumes of water which it delivered. Table II shows the figures obtained in this calibration, and the corrected volumes shown were, of course, used in all calculations. As is indicated in column 2 of Table II the burette could be read accurately to 0.01 ml. since every 0.10 ml. was marked, and the distance between any two successive marks was about 6 mm..

Table/

Table II

Calibration of 5 ml. Burette.

Weight of H_2O delivered.	Apparent volume	Actual volume	Correction
3.7992 gm.	3.80 ml.	3.806 ml.	+ 0.006 ml.
3.9901 "	4.00 "	4.002 "	+ 0.002 "
4.0927 "	4.10 "	4.100 "	0.000 "
4.1979 "	4.20 "	4.206 "	+ 0.006 "
4.2956 "	4.30 "	4.304 "	+ 0.004 "
4.3836 "	4.40 "	4.392 "	- 0.008 "
4.5862 "	4.60 "	4.595 "	- 0.005
Temperature = 15° C.			

In the last column of Tables III and IV are given values for the concentration of un-neutralised acid which have been calculated from the following formula:-

E.M.F.(millivolts) = 446.1 + 59.1 × log 'c'

where 'c' is the concentration of un-neutralised acid.

The "actual" concentration of un-neutralised acid is calculated from the volumes and normalities of the acid and alkali used in making up the calibration mixtures. Comparison of the "calculated"figures with the figures for the "actual" acid concentration shows that the formula is accurate generallt to within 3% and at worst to within 6%.

Concentrations/

Concentrations of salts employed in calibration of the electrode(see Table IV) are similar to those present in the ultrafiltrates (Tables IX b, c,& d.).

Table IV shows that these salts are without influ-:ence on the E. M. F. when present in the concentrations employed. Duplicate experiments showed that individual values were all constant, although in a number of cases, periods of several weeks elapsed between duplicate determinations. This served to demonstrate also that the cell was behaving normally during the course of the investigation.

Calibration of Electrode

Table III

Composition of mixtures = 2 ml. HCl (0.01498 N.)
+ 'X' ml. NaOH (0.00627 N.)

Volume 'X' NaOH (0.00627N)	Observed E. M. F. (millivolts)	Mean E.M.F.	Concentration unneutralised acid. (Micromols per litre)	
			Actual	Calculated
3.806 ml.	269.5 268.5 269.1 269.5	269.2	1053	1016
4.002 "	262.2 262.1 262.1 261.7 261.5	261.9	813	764
4.206 "	254.0 254.5 254.5	254.3	582	569
4.304 "	250.6 249.3	250.0	474	481
4.392 "	245.5 245.1 246.0 246.1	245.7	382	407
4.595 "	225.5 225.0 225.5 225.0	225.3	177	184

Calibration of Electrode (continued)

Table IV

Composition of mixtures = 2 ml. HCl (0.01498 N.)
+ 'X' ml. NaOH (0.00627 N.)
+ (2 + 'X') ml. water or salt soln.

Volume 'X' NaOH (0.00627N)	Salt	Final concn. salt. (milli-equiv. /litre)	Observed E. M. F. (milli-volts)	Concentration unneutralised acid. (Micromols per litre)	
				Actual	Calculated
	H_2O	-	240.9		
	"	-	241.0		
4.100 ml.	LiCl	61.5	241.0		
	"	"	240.8		
	"	200.0	242.5		
			mean 241.2	349	342
	H_2O	-	236.2		
	"	-	236.1		
4.206 ml.	LiCl	61.5	236.0		
	"	"	236.2		
	"	200.0	236.0		
			mean 236.1	291	280
	H_2O	-	230.6		
4.304 ml	"	-	232.4		
			mean 231.5	237	234

(table concluded overleaf)

Table IV (continued)

Composition of mixtures = 2 ml. HCl (0.01498 N.)
+ 'X' ml. NaOH (0.00627 N.)
+(2 + 'X') ml. water or salt soln.

Volume 'X' NaOH (0.00627N)	Salt	Final concn. salt (milli-equiv. /litre)	Observed E. M. F. (milli-volts)	Concentration unneutralised acid. (Micromols per litre)	
				Actual	Calculated
4.392 ml.	H_2O	-	227.3		
	"	-	227.3		
	"	-	226.4		
	LiCl	61.5	227.0		
	$BaCl_2$	0.678	227.3		
	"	"	227.5		
	$Nd(NO_3)_3$	2.7	225.8		
	"	"	226.5		
	"	0.532	226.9		
	"	"	227.4		
			mean 226.9	191	195

Reagent Solutions.

All salt solutions were kept in Jena glass bottles which had been washed and steamed out before use. Where possible the solutions were made up or diluted to the required strengths in Pyrex standard flasks.

Lithium chloride was obtained as the 'anhydrous' salt from British Drug Houses Ltd., and was twice recrystallised from water before use. Crystals of lithium chloride (LiCl) rapidly absorb moisture from the atmosphere thus making it difficult to weigh accurately a required quantity. An approximately decinormal solution was therefore made up and carefully standardised by titration with a solution of silver nitrate of known strength.

Barium chloride crystals ($BaCl_2,2H_2O$) of 'Analar' quality were used without further purification for preparation of the barium chloride solutions.

A small quantity of neodymium nitrate crystals was obtained from B. D. H.Ltd.. These crystals - formula $Nd(NO_3)_3,6H_2O$ $\therefore$ M.W. = 438.396 - were of a uniform purple-pink colour, and as the available quantity was limited and the sample appeared to be quite pure, this salt was used without any special purification.

RESULTS.

Coagulation Experiments (Nephelometric Values)

Results for the first series of coagulation experiments (see page12) are given in Table V.

Table V.

Temperature = 18° C.

Final concentration of Salt (milliequivalents / litre)	Nephelometric Values with ⊛	
	Barium chloride	Neodymium nitrate
0.500	508	505
0.667	508	504
0.833	464	317
0.909	362	244
1.000	145	84.7
1.053	54	19.6
1.111	33.9	15.3
1.250	24.5	9.8
1.667	17.2	9.6
2.500	9.0	9.2

⊛ see page 19

Results for the other series of coagulation experiments (see page 14) are given in Tables VI and VII. Each figure for the nephelometric value represents, in the great majority of cases, a completely independent determination.

Table VI

Temperature = 0° C.

Final concn. of salt (milli-equiv./litre)	Nephelometric Value* after			
	0 hours	½ hour	1 hour	2 hours.
Lithium Chloride				
50	-	505	-	-
150	-	505	505	-
200	-	551 553	553	-
250	-	592	-	-
Barium Chloride				
0.500	-	-	-	505
0.667	505 508	-	-	506
0.678	541 549	549	548	-
0.682	588	-	-	-
0.690	610 617	-	-	-
0.698	667	-	-	-
0.714	676	-	-	680
0.769	826	-	-	826

* see page 19

(table concluded overleaf)

Table VI (concluded)

Temperature = 0° C.

Final conc. salt, milli-equiv/litre.	Neodymium Nitrate			
	Nephelometric Value* after			
	0 hours	½ hour	1 hour	2 hours.
0.475	-	505	505	-
0.500	505 513 512	-	-	505
0.532	544	544	-	-
0.549	-	572	-	-
0.588	-	621	-	-
0.667	719 730	-	-	719

Table VII.

Temperature = 18° C.

Final salt concn. milli-equiv./litre	Barium Chloride			
	Nephelometric Value* after			
	0 hours	½ hour	1 hour	2 hours.
0.714	505	-	505	-
0.769	548	-	548	-
	Neodymium Nitrate			
0.714	694	694	-	-
0.769	1811	1811	1811	1811

* see page 19

Table VIII

Sol + Equal Volume of Water.

Date	Temperature	Nephelometric Value ⊛
15/6/36.	18 °C.	500
27/6/36.	18 "	505
27/6/36.	18 "	505 ⊕
7/9/36.	18 "	505
7/9/36.	18 "	505
8/3/37.	0 "	504

⊛ see page 19
⊕ filtered through Jena sintered glass filter - porosity 5/3.

Ionic Interchange (Replacement Values)

The data showing the replacement of hydrogen ion in the sulphur micelles by the cation of added salts are given in Tables IX b, c, and d.

'X' is the volume of sodium hydroxide (0.00627 N.) added to 2 ml. ultrafiltrate, and 'c' is the concen-:tration of un-neutralised acid present in the mixture as calculated from the E.M.F. by the formula given on page 28.

The total concentration (normality) of acid in the ultrafiltrate itself is therefore given by the follow-:ing formula:-

$$\frac{(2 + 'X') \times 'c' \quad + \quad 0.00627 \times 'X'}{2}$$

The/

The concentration of acid liberated by ionic interchange (the "Replacement Value") is obtained by subtracting the total concentration of acid in the ultrafiltrate for sol + water (Table IX a), from the total concentration of acid in the ultrafiltrate for sol + salt.

Use of the above formula gives the acid concen-:tration as a normality. In the tables, however, these concentrations are expressed as micro-equivalents per litre.

A small amount of coarse sulphur had been present in the sol from the beginning, but, towards the conclusion of the work, when the volume of sol became small, it was thought that there was a risk of drawing this coarse sulphur into the pipette when withdrawing a volume of sol. For this reason the sol was filtered through an ordinary filter paper, and values marked '⊛' in Table IX b and IX d were obtained with this filtered sol. The filtration obviously removed some of the intermicellar acid (as is indicated by the lower E.M.F. values). Replace-:ment values given in these cases are therefore deduced on the assumption that the total concentration of acid in the ultrafiltrate for sol + water was

14229 micro-equivalents per litre.

Table/

Table IX a

Sol + Water.

'X'	E.M.F. milli-volts.	'c'	Total concentration of acid in original ultra-filtrate.
4.002 ml.	259.9	706	14664.
"	260.0	710	14676
4.464 ml.	233.5	254	14816
"	233.0	248	14797
			Mean value 14738

Replacement Values.

Table IX b.

Sol + Lithium Chloride.

'X'	E.M.F.	'c'	Total conc. acid in ultra -filtrate.	Replacement Value.
Final concentration LiCl = 150 milliequiv. per litre.				
4.464 ml.	242.8	363	15168	430
	244.0	380	15224	486
4.649 ml.	180.6	32	14682 ⊛	453
	179.0	30	14675 ⊛	446
Final concentration LiCl = 200 milliequiv. per litre.				
4.464 ml.	243.5	372	15197	459
	243.9	378	15217	479
4.649 ml.	192.3	51	14744 ⊛	515
	189.6	46	14727 ⊛	498

⊛ see page 38

Table IX c.

Sol + Barium Chloride.

Final concentration $BaCl_2$ = 0.667 milliequiv./litre.				
'X'	E.M.F.	'c'	Total conc. acid in ultra -filtrate.	Replacement Value.
4.464 ml	244.8	393	15265	527
	244.4	386	15243	505
Final concentration $BaCl_2$ = 0.678 milliequiv./litre.				
4.464 ml	242.2	(356)	(15146)	(408)
4.649 ml	228.3	206	15260	522
	227.8	202	15247	509

Table IX d.

Sol + Neodymium Nitrate.

Final concentration $Nd(NO_3)_3$ = 0.475 milliequiv./litre				
'X'	E.M.F.	'c'	Total conc. acid in ultra -filtrate.	Replacement Value.
4.649 ml	224.9	181	15177	439
	225.7	187	15197	459
Final concentration $Nd(NO_3)_3$ = 0.532 milliequiv./litre				
4.464 ml	243.9	378	15217	479
	244.3	385	15240	502
Final concentration $Nd(NO_3)_3$ = 10.0 milliequiv./litre.				
4.464 ml	242.8	363	15168 ⊛	939
	244.1	382	15230 ⊛	1001
4.649 ml	238.4	306	15592	854

⊛ see page 38

Preparation of Stearic Acid Sol.

A slightly modified form of the method due to Iyer and Iyengar (1) was found - after considerable experiment - to give a stearic acid sol of satisfact-:ory stability and properties.

Excess of 'Schuchardt's' extra pure stearic acid was shaken with "Analar" methyl alcohol at room temperature (about 16° C.), and the saturated alcoholic solution of stearic acid separated from the undissolv-:ed acid by filtration through a Jena No 1 sintered glass filter. To 25 ml. of this saturated solution was added 25 ml. of "Analar" methyl alcohol, and the mixture cooled in ice to as low a temperature as possible without precipitation of solid stearic acid (approximately 6° C.). This alcoholic stearic acid solution was now added very slowly to 175 ml. boiling distilled water (p_H of water by B.D.H. universal indicator = 6.5) contained in a large Jena glass beaker. It was found most convenient and satisfact-:ory to make this addition by means of a specially made "dropping funnel" - a pyrex tube (about 50 ml. capacity) one end of which was drawn off to give a fine capillary. Addition of the alcoholic solution was thus made in a constant slow stream - about seven minutes/

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(1) Iyer and Iyengar, Half-Yearly Journal of the Mysore University, Vol. VI (1932) 1 p.16.

minutes were required to complete the addition of the 50 mls.. After the addition of about 2 ml. of alcoholic solution a slight turbidity appeared in the water which was stirred constantly and maintained just at its boiling point. When the addition of the alcoholic solution of stearic acid was complete, the sol was boiled (gently) for 20 minutes to remove all methyl alcohol. Water lost by evaporation during this boiling was replaced continuously by addition from the dropping funnel (described above) which was filled with boiling distilled water. After cooling the sol was stored in a Jena glass bottle.

Sols prepared as described (volume about 200mls.) had, when cold, a bluish translucent appearance. They were quite stable, and could be shaken, or drawn into the pipette without coagulation taking place. The production of a streaky appearance - the "Schlieren" effect - when the sol is made to rotate gently in the bottle is not very pronounced in the case of these sols.

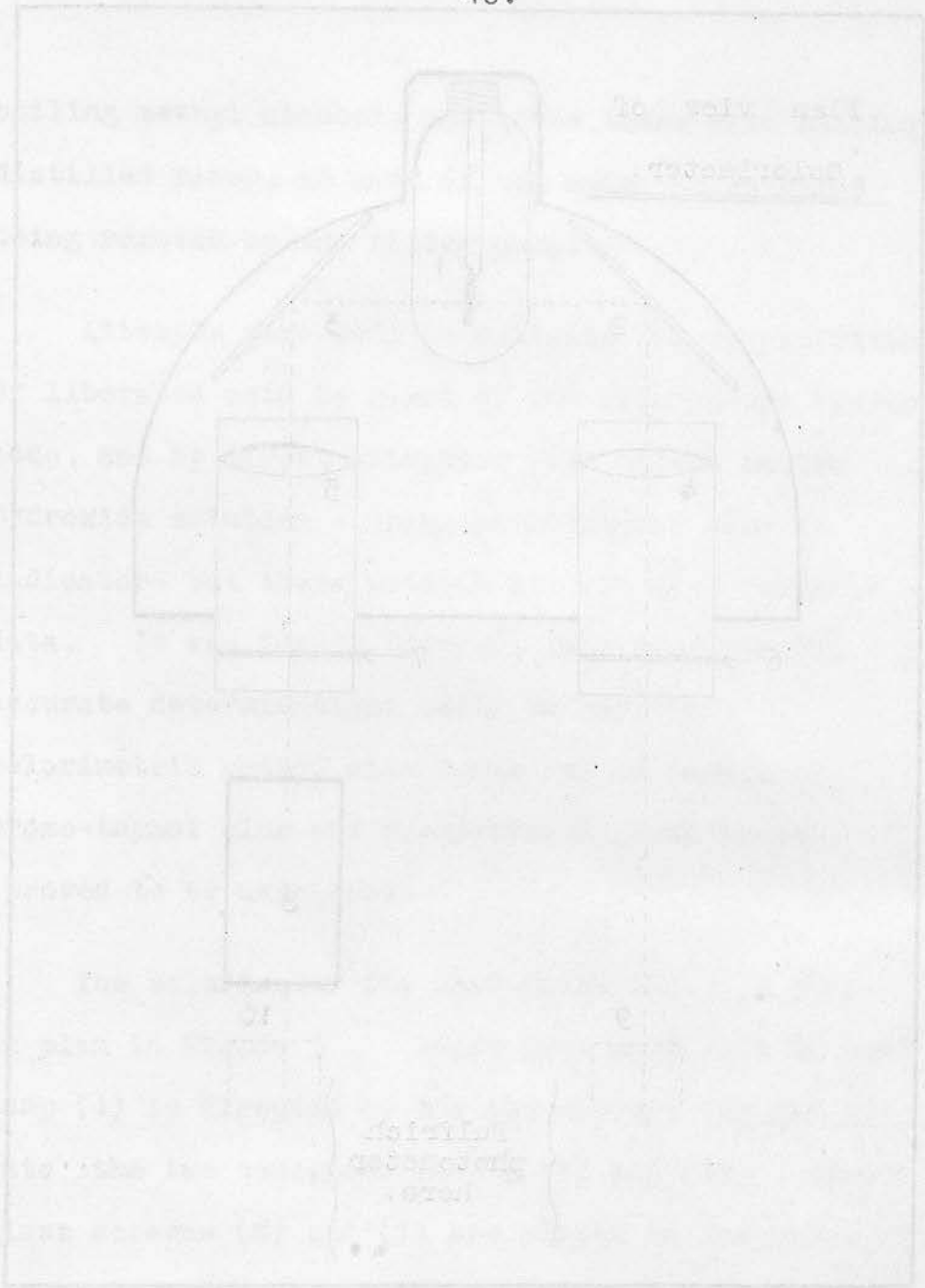
Departure from the foregoing conditions resulted in the production of a sol or suspension which had a dense white appearance and was very easily coagulated by shaking or drawing the liquid into a pipette. In these/

these sols or suspensions the "Schlieren" effect is very pronounced - due possibly, to the presence of comparatively large particles of stearic acid.

Although these dispersions are very unstable when freshly prepared, there is a marked increase in stability after a period of about a week. During this period of standing a certain amount of floccul-:ation appears to take place. The coagulum, however, does not rise to the surface in the usual manner of solid stearic acid, but settles to the bottom of the vessel in which the sol is stored.

Determination of Ionic Interchange.

The following procedure was adopted to determine the replacement values in the case of the stearic acid sol. Equal volumes (10mls.) of sol and salt solution were introduced into a small Jena conical flask, the mixture allowed to stand for 10 minutes, and then filtered through a No. 4 Jena sintered glass filter. This filter removed all the stearic acid, whether coagulated or not. In every case the first 2 mls. of filtrate were rejected - 10 mls. were requir-:ed for each acid determination by the colorimetric method described below. Before each filtration the glass filter was cleaned by washing, once with boiling/



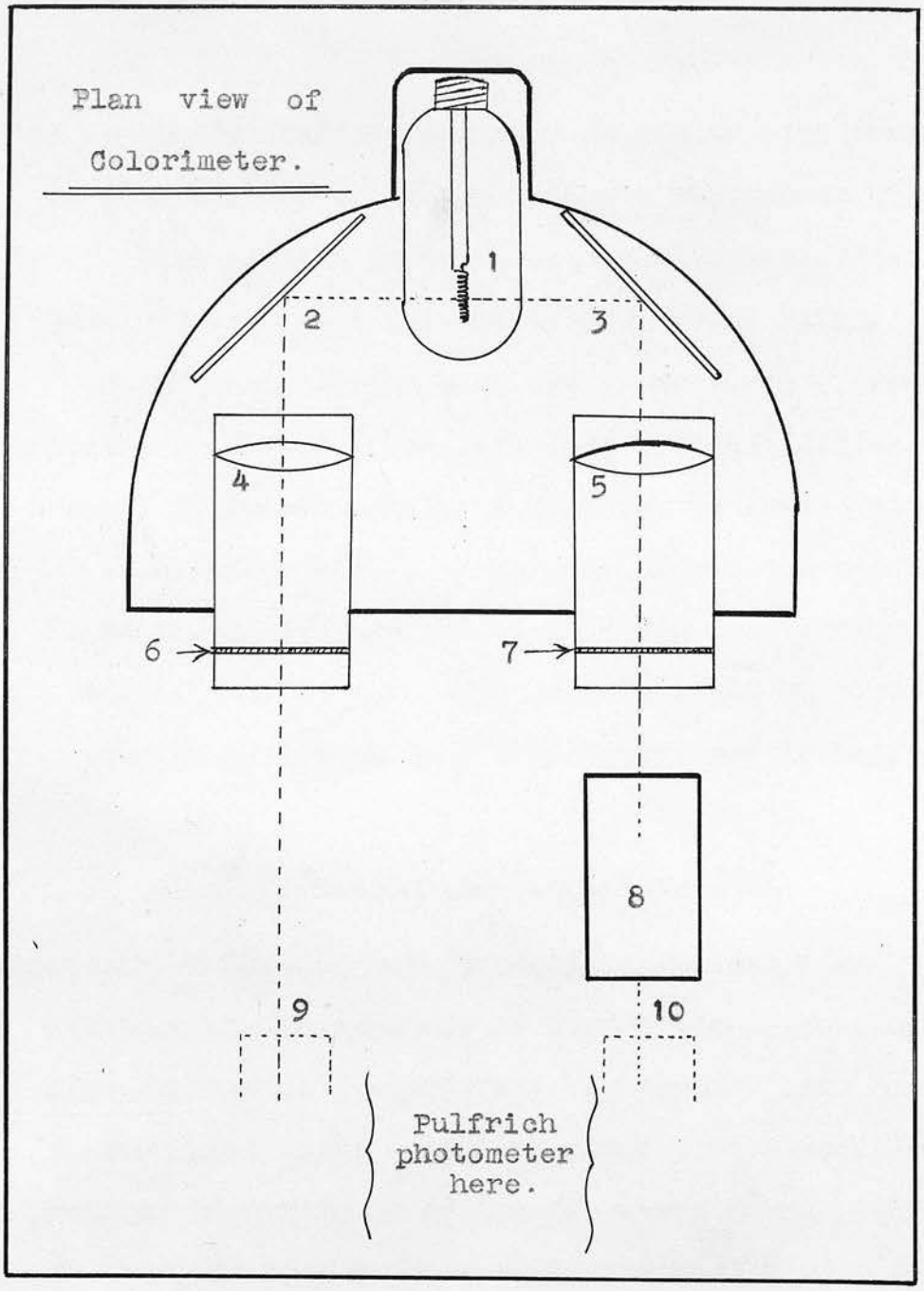

Plan view of
Colorimeter.
1
2
3
4
5
6
7
8
9
10
Pulfrich
photometer
here.

Figure 5.

boiling methyl alcohol, and three times with boiling distilled water, as much of the water as possible being removed by the filter pump.

Attempts were made to estimate the concentration of liberated acid by means of the quinhydrone electr-:ode, and by direct titration with dilute barium hydroxide solution - using bromo-thymol blue as indicator- but these methods did not give reliable data. It was found, however, that sufficiently accurate determinations could be made by a colorimetric method with Congo red as indicator, bromo-thymol blue and bromo-cresol green having proved to be unsuitable.

The colorimeter (by Carl Zeiss Ltd.) is shown in plan in Figure 5 . Light from an 8 volt 30 watt lamp (1) is directed by the two mirrors (2) and (3) onto the two condenser lenses (4) and (5). Ground glass screens (6) and (7) are placed in the paths of the light beams, as shown, to increase the intensity of illumination.

Ten mls. of 'test' solution were placed in the rectangular cell (8) along with 20 drops Congo red indicator (0.1% aqueous solution). The intensities of/

of the two light beams at (9) and (10) were examined by means of the Pulfrich photometer, which is described in detail and shown diagramatically on pages 16 to 18. When using the photometer in conjunction with the colorimeter, the right-hand drum (i.e., the drum controlling the size of the aperture through which passes the light emerging from the cell (8) containing the coloured 'test' liquid) was set at '74' and was never altered from this setting. The left-hand drum was now adjusted until equal brightness was obtained in both halves of the field of vision in the photometer. Both beams of light passed through an orange filter No. S 61 placed at (4) in Figure 2 - facing page 17.

The method was calibrated - and the reproducibility of results checked - by measurements with mixtures consisting of 'x' mls. HCl (0.0001068 N.) and(10 - x) mls. of either water, N/2 KCl or N KCl. Over the range of acid concentrations concerned in the stearic acid investigation, the (left-hand) drum readings were found to vary in a linear fashion with the acid concentration, and to be quite independent of the concentration of KCl, as is shown by the calibration data in Table XIII and Figure 9.

The/

The concentrations of the sols were determined by drying a known volume of sol to a constant weight in an air oven at 97° C.. Values obtained in this way were as follows:-

Sol A . .	1.23 gms. stearic acid per litre.
Sol C . .	1.385gms. stearic acid per litre.

Coagulation Experiments.

A mixture of equal volumes of sol and water when filtered through a No.3 Jena sintered glass filter gave (in contrast to No. 4 filter) a filtrate which obviously contained colloidal material. Mixtures of sol and salt solution of increasing concentration were made up and filtered through the No. 3 filter, until a concentration of salt was found which gave a filtrate containing no colloid. It was found possible to determine the coagulation value quite accurately by simple inspection of the filtrates, so that recourse to the nephelometer or similar instrument was unnecess-:ary.

Table XIV illustrates how the replacement value increases with 'ageing' of the sols. The influence of the concentration of the added salt is shown in Table XV and Figure 10. Coagulation observations are record-:ed in Table XVI. The results shown in Table XVII and Figure 11 were obtained by diluting sol 'C' with water before adding - to the diluted sol - an equal volume of normal potassium chloride solution.

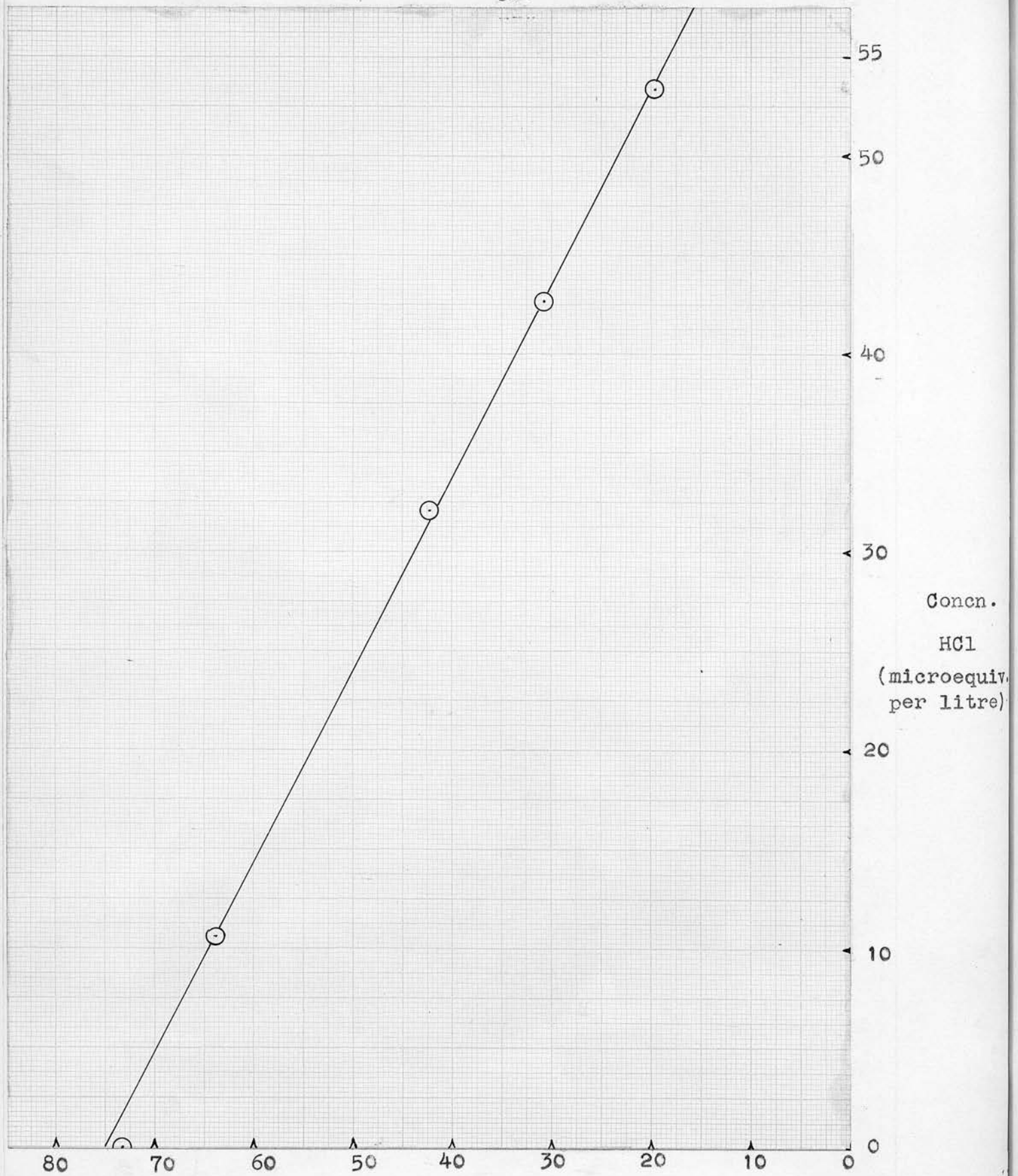


Figure 9.

Calibration of Colorimeter.

Calibration of Colorimeter.

Table XIII

'x'	Drum Readings*				Concn. HCl (microequiv. per litre)
	a	b	c	Mean	
0.0	72.8	73.5	-		
	73.3	74.0	-		
	73.0	73.5	-		
	mean 73.0	mean 73.7	-	73.4	0.00
1.0	63.8	63.6	64.2		
	64.0	64.2	64.0		
	63.5	64.1	63.5		
	mean 63.8	mean 64.0	mean 63.9	63.9	10.68
3.0	42.0	42.0	42.8		
	42.5	42.5	42.0		
	41.9	42.5	42.2		
	mean 42.1	mean 42.3	mean 42.3	42.2	32.04
4.0	30.0	30.5	31.0		
	30.5	30.3	30.8		
	30.9	30.7	31.2		
	mean 30.5	mean 30.5	mean 31.0	30.7	42.72
5.0	-	19.4	-		
	-	19.8	-		
	-	19.7	-		
	-	mean 19.6	-	19.6	53.40

* a, b, and c denote that the solutions were made up with (10 - x) mls of H_2O, $\frac{N}{2}$ KCl, and N. KCl respectively.

Table XIV

Influence of Time on Replacement Value.

Sol	Time from preparation (hours)	Drum readings	Concn. liberated acid. (microequiv. per litre)
A	3	74.0	0.0
	24	35.6 35.0 (mean 35.3)	38.2
	48	36.1	37.5
B	0	74.0	0.0
	96	36.2 36.6 (mean 36.4)	37.1

Table XV

Sol A - Influence of Salt Concn. on Replacement Value.

Final concn. KCl (milliequiv. per litre)	Drum readings			Concn. liberated acid. (microequiv. per litre)
	Expt. 1	Expt. 2	Mean	
0.0	73.8	73.8 ⊛	73.8	0.0
62.5	58.0	58.0	58.0	16.2
77.5 #	54.7	54.9	54.8	19.2
125.0	50.2	50.3	50.3	23.7
250.0	45.0	45.0	45.0	28.7
500.0	36.1	35.6 35.0	35.6	37.9

⊛ Sol B

\# Coagulation Value.

Table XVI

Coagulation Observations.

Final concentration Potassium Chloride (milliequiv./litre)	Appearance of Filtrate (No. 3 Jena sintered glass filter)
0.0	Colloidal
62.5	Colloidal
75.0 ⊛	Colloidal
80.0 ⊛	Quite clear
85.0	Quite clear

⊛ Duplicated with the same result.

Table XVII

Sol C - Influence of Sol Concn. on Replacement Values.

Concn. of Stearic acid in mixture. (gms./litre)	Drum readings			Concn. of acid liberated by N/2 KCl (microequiv. per litre)
	Expt. 1	Expt. 2	Mean	
0.693	33.3	33.2	33.3	40.2
0.346	43.6	43.8	43.7	29.9
0.173	56.0	56.2	56.1	18.0
0.139	59.8	59.9	59.9	14.4
0.087	65.3	65.3	65.3	9.2
0.069	66.9	66.8	66.9	7.8

D I S C U S S I O N.

Sulphur Sol.

It will be convenient to consider in the first place, the data for the coagulation of the sulphur sol at 0° C. given in Table VI (pages 35 and 36), and reproduced in Figures 6 and 7 . The object of these experiments was to determine the concentration of lithium chloride, barium chloride and neodymium nitrate which just failed to produce coagulation - i.e., the "threshold values" of these salts. Since the coagulation of colloidal sulphur is influenced to an exceptional extent by the temperature, it was necessary to keep this constant in order to secure strictly comparable figures. It was decided to work at 0° C. because of the ease with which this temperature could be maintained in the nephelometer, and also during the ultrafiltrations involved in the determination of the ionic interchange.

It will be seen from Table VIII (page 37) that the nephelometric value for the sol after dilution with an equal volume of water was constant over a long period of time, and that the value was the same (505) at 0° C. as at 18° C.. these results show that the/

the sol was very stable and that no coagulation occured at 0° C. in the absence of added electrolyte.

In these experiments the coagulated sulphur was not removed by filtration prior to the nephelometric determination. Its presence could not be detected by the unaided eye, but it produced an intensification of the scattered light so that the nephelometric value was increased. Moreover, the coagulated sulphur showed no tendency to settle out, but formed a stable suspension under the conditions of the experiment. This follows from the observations (see Tables VI and VII - pages 35 and 36) that the nephelometric value remained constant for a period of at least two hours from the time of mixing the sol with the salt solution.

The absence of variation in the nephelometric value with time at all concentrations of the salts employed also shows that no coagulation process was involved which possessed a velocity measurable under the given conditions. It is well known ① that, owing to their polydisperse character, sulphur sols undergo "fractional" coagulation, the coarser particles being coagulated at concentrations of electrolyte lower/

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① Odén, Nova Acta Upsala IV, 3 (1913) 156
Also references on page 5.

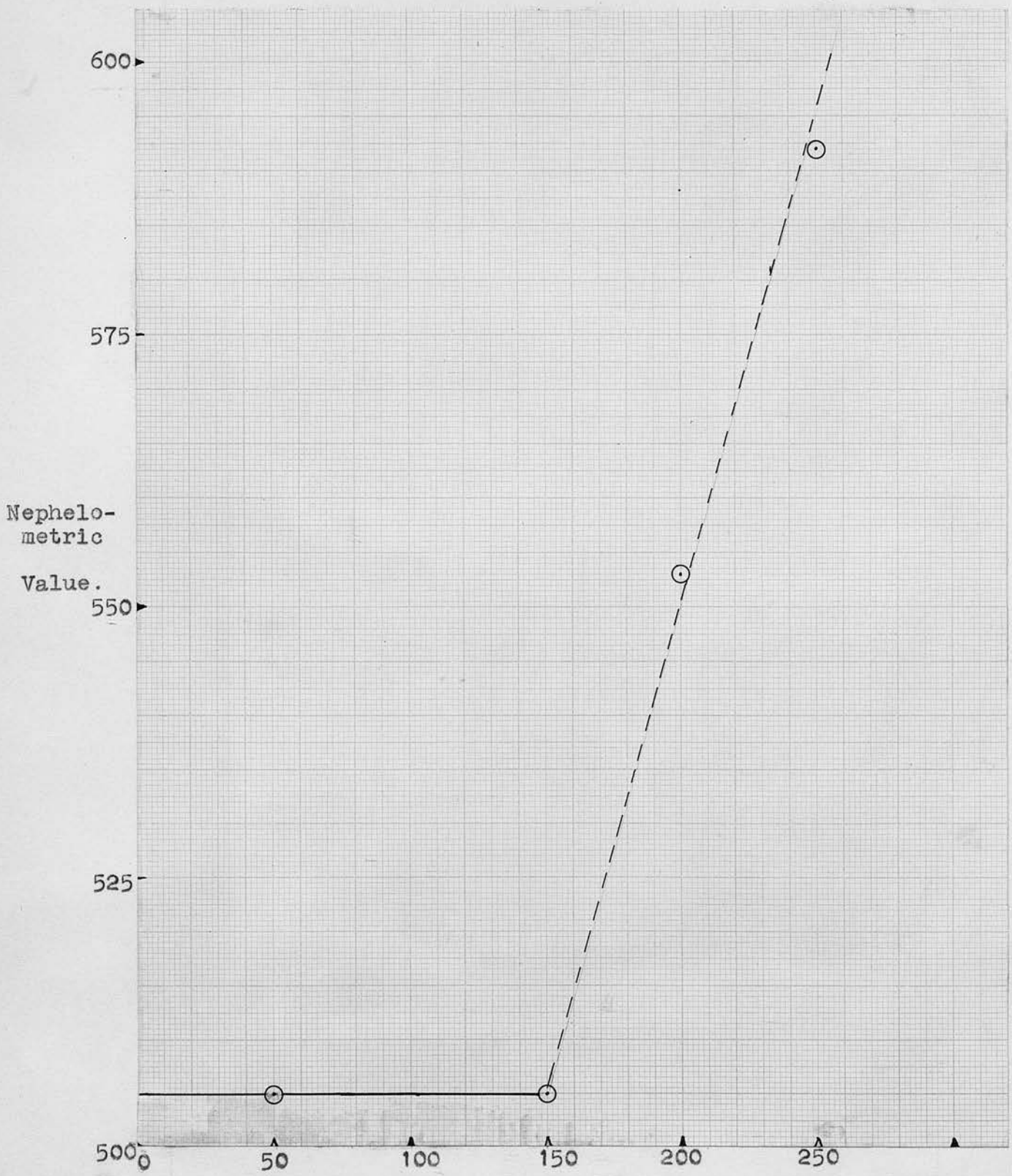
600
575
Nephelo-
metric
Value.
550
525
500
0
50
100
150
200
250
Final concentration of Lithium Chloride
(milli-equivalents per litre)

Figure 6.

lower than those which are necessary to coagulate the finer particles. Hence the present data establish that the coagulation of each fraction is a rapid process, being complete almost as soon as the coagulant is all added.

Initially it was thought feasible to obtain comparable "coagulation values" for the three salts by determining the concentration required to give a certain fixed increase in the nephelometric value above that for the uncoagulated sol. The necessary condition was that the nephelometric value should bear the same relation to the degree of coagulation in all three cases. That actually this is not so will be clear from a consideration of Figures 6 & 7. It will be seen that while in the case of each salt the nephelometric values lie roughly on a straight line, the slope of the neodymium nitrate line is quite definately less than that for the barium chlor-:ide. This implies that if a given nephelometric value represents the same degree of coagulation, then a given increment in the concentration of barium chloride produces a greater amount of coagulation than the same increment in the concentration of neodymium nitrate. This cannot be the fact, since the neodymium/

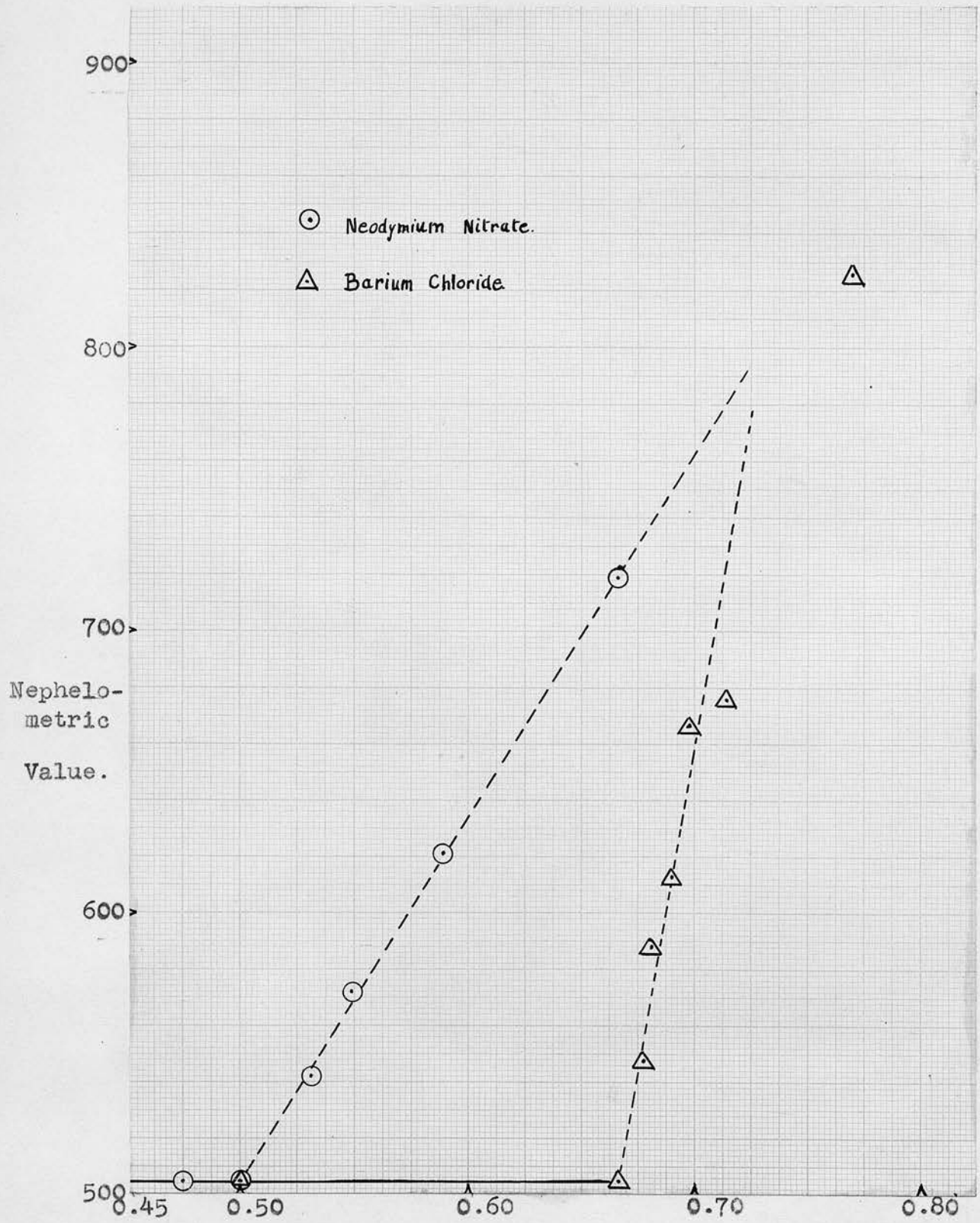
900
800
700
600
500
Nephelo-
metric
Value.
Neodymium Nitrate.
Barium Chloride
0.45
0.50
0.60
0.70
0.80
Final concentration of Salt
(milli-equivalents per litre)

Figure 7.

the neodymium salt is obviously the more powerful coagulant; coagulation commencing at a considerably lower concentration with this salt than with barium chloride.

It is not possible to do more than suggest reasons for the difference in the intensity of scattering produced by the aggregates in the case of barium chloride on the one hand, and of neodymium nitrate on the other. Probable factors are the size and hydration of the aggregates. It is certainly the case that sulphur coagula differ in their proper-:ties.[1] Thus the coagula produced by salts of lithium, sodium and certain other metals are readily peptised when the excess of coagulant is washed out, whereas other coagula, including that of barium cannot be peptised. There does not appear to be any definite information with regard to the behaviour of neodymium coagulum in this connection. However, Bassett and Durrant [1] state that "owing to the nature of the neodymium and thorium gels (i.e. coagula), they are exceedingly difficult to wash thoroughly/

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① Bassett & Durrant, J.C.S., 1931, 2919; Odén, loc. cit. page 55; Weiser & cunningham, Colloid Symposium Monograph VI (1928) 319.

thoroughly. . . .", whereas no mention is made of similar difficulty with barium coagulum, which was also studied. This observation at least indicates a difference in the state of aggregation.

In view of the foregoing the most satisfactory method of comparing the coagulating powers of the three salts was to determine the "threshold values", i.e. to ascertain the respective concentrations which were just sufficient to raise the nephelometric value above that for the uncoagulated sol, (505).

Table X (page 61) contains the values obtained. The value for lithium chloride is given as 150 milli-equivalents per litre. It will be seen from Table VI (page 35) that the true value cannot be less than this and if greater, cannot be as great as 200 milliequiv. per litre. The value for barium chloride is given as 0.673 - (the mean of 0.667 and 0.678 - Table VI p. 36), which must be very nearly correct. Also the value of 0.500 for neodymium nitrate cannot be far out, although the nephelometric value perhaps shows a tendency to be slightly higher than that for the uncoagulated sol.

Table X/

Table X

Salt	Threshold value. (milliequiv. per litre)	Replacement value. (microequiv. per litre)	Degree of Ionic Interchange.
LiCl	150	453	0.49
$BaCl_2$	0.673	516	0.56
$Nd(NO_3)_3$	0.500	470	0.51

The experiments on ionic interchange (at 0° C.) have now to be considered. Previous work ① with sulphur sols has shown that these systems are stabil-:ised by the adsorption of polythionic acid (probably hexathionic acid) on the surface of the particles. Thus the double layer consists of an inner fixed stabilising layer of polythionate anions (giving a negative charge to the particle) and an electrically equivalent outer layer of mobile hydrogen ions. On introducing a salt into the sol, these hydrogen ions interchange with the salt kations, to an extent depending upon the nature and concentration of the latter, so that there is an increase in the acidity of the intermicellar liquid.

The object of the present experiments was to determine the replacement values of lithium chloride, barium chloride and neodymium nitrate, at their respective threshold values; that is to say, to measure the increase in the concentration of inter-:micellary acid produced by each salt when present at the concentration which was just sufficient to coagulate the coarsest particles of the sol. In the/

① Freundlich & Scholz, Koll. Beih., 16 (1922) 234.
Bassett & Durrant, loc. cit. p. 59.
Bolam & Muir, J.C.S.(1933) 1022.

the third column of Table X will be found the required replacement values which were deduced from the actual experimental data as follows. In the case of lithium chloride the required value is the mean of the four values directly obtained for a concentration of 150 m.e./l. ⊛ as given in the upper half of the last column in Table IX b (p.40). The value given for barium chloride is the mean of the four values in the last column of Table IX c (page 41). That taken for neodymium is deduced on the assumption that the replacement value at 0.500 m.e./l. will be the mean of the replacement values for 0.475 and 0.532 m.e./l., i.e., the mean of the first four values in the last column of Table IX d (page 42). Justification for this assumption lies partly in the relatively narrow range of concentrations concerned and also in the fact that previous work has shown that at the degree of interchange involved, the replacement is generally proportional to the concentration of salt.

It is certain that the replacement was complete in the presence of 10 m.e./l. of neodymium nitrate (see later, page 74), which gave a replacement value of 931 (mean of the last three values in the last column of Table IX d - page 42). The figures in the/

⊛ m.e./l. = milli-equivalents per litre.

the fourth column of Table X were obtained by dividing the figures in the third column by 931, and hence represent the degree of ionic interchange in each case, (complete interchange = 1.00).

Since the threshold value is only very slightly less than the concentration required to produce the first sign of coagulation, it follows that, for all practical purposes, the data obtained as described in the foregoing gives the degrees of ionic interchange for the three salts at concentrations producing the same degree of instability in the sol.

Weiser and Gray (1) have investigated the interchange in a (Raffo) sulphur sol prepared by the same method as that employed in the present instance, and also in a (Selmi) sol prepared by passing hydrogen sulphide and sulphur dioxide simultaenously into water previously saturated with sulphur dioxide. According to the manner in which Weiser and Gray interpret their data, the degrees of interchange at the point of complete coagulation (i.e. maximum instability) were as follows:-

Table XI/

(1) Weiser and Gray, J. Phys. Ch., 39 (1935) 1163.

Table XI (*)

Salt	Degree of Interchange	
	Raffo Sol	Selmi Sol (#)
$BaCl_2$	1.00	0.96
$SrCl_2$	1.00	0.93
$NdCl_3$	0.65	0.71
$AlCl_3$	0.69 (#)	0.71
$ThCl_4$	0.58	0.71
$CrCl_3$	-	0.85

(*) Room temperature - apparently.

(#) Taken from Weiser and Gray's graphs; the actual figures are not stated in the paper.

Weiser and Gray conclude that "In contrast to the behaviour of the alkaline earth kations, thorium, neodymium and aluminium coagulate the sol before the maximum displacement of hydrogen ion is attained, indicating further ionic interchange after the charge on the particles has been reduced to the point of coagulation" and "Contrary to the view of Bolam and Muir, the displacement of hydrogen ion is not the same at the coagulation point - - - - - much less hydrogen is displaced at the precipitation value of neodymium than at the precipitation value of barium/

barium".

The degrees of interchange calculated from the replacement data of Bolam and co-workers are as follows:-

Table XII

Salt	Degree of Interchange for complete coagulation. ①②③
LiCl	0.98 -1.00
NaCl	0.95
KCl	0.98, 0.89, 0.95, 0.89, 1.00, 0.97, 0.97⊛
RbCl	0.95
NH_4Cl	0.94
NH_4I	0.92
$BaCl_2$	0.92, 0.88 - 0.93.
$CaCl_2$	0.97
$AlCl_3$	0.95
	Degree of Interchange for a given amount of partial coagn.. ③
LiCl	0.85
KCl	0.87
$SrCl_2$	0.82

⊛ Temp.= 0°C. Room temperature in all other cases.

① Bolam & Bowden, J.C.S., 1932, 2684.
② Bolam & Muir, loc. cit. page 62.
③ Bolam & Muir, J.C.S., 1934, 1754.

These figures indicate that under comparable conditions, aluminium chloride produces the same degree of interchange as the salts of the alkali metals and those of the alkaline earth metals. It would appear that the results of the present work also substantially support the view that salts with polyvalent kations do not behave exceptionally in regard to the relation between interchange and coagulating action. From Table X (page 61) it will be seen that the average value for the degree of interchange is 0.52, and that the variation from the mean amounts to -6% for lithium chloride, +8% for barium chloride, and -2% for neodymium nitrate. A considerable proportion of the variation can certainly be attributed to experimental error in view of the difficulty of the experiments. Indeed the whole of the variation may well be due to this cause, since in previous work (Table XII - page 66) barium, strontium and calcium gave the same interchange as the alkali metals under comparable conditions, so that lithium and barium might be expected to show equal replacement in the present case.

The present data certainly do not confirm the figures in Table XI. According to Weiser and Gray, the interchange/

the interchange for neodymium (0.65) is less than that for barium (1.00) by 35% in the case of the Raffo sol; the corresponding difference for the Selmi sol being 26% ($BaCl_2$ - 0.96: $NdCl_3$ - 0.71). On the other hand, even supposing the data in Table X to be correct as they stand, they show that the interchange for neodymium (0.51) was less than 9% below that for barium (0.56).

It can be shown that the coagulation experiments at 18° C. also offer support for the view that neodymium is unexceptional. Table VII (page 36) gives nephelometric values, at the above temperature, obtained in the same manner as in the experiments at 0° C.. It will be seen that 0.769 m.e./l.(#) barium chloride at 18° C. gives the same nephelometric value as 0.678 m.e./l. at 0° C. (Table VI - page 35).(*) Since the same salt is concerned it seems very probable that the identity in nephelometric value signifies the same degree of coagulation in the two cases. Now Bolam and Muir (reference (3) - page 66.) have shown that the degree of interchange for complete coagulation by potassium chloride is the same at 0° C. and 16.5° C., although the coagulating concen-

:trations/

(#) m.e./l. = milli-equivalents per litre.

(*) The sol thus showed normal behaviour in that it was more easily coagulated at the lower temperature.

:trations of the salt are very different. Assuming, in the absence of evidence to the contrary, that in the present instance also, the degree of interchange is the same for the same degree of coagulation, irrespective of temperature, it follows that the replacement value for 0.769 m.e./l. barium chloride is 516 micro-equivalents per litre at 18° C. (Table IX c - page 41). Hence the "equilibrium" concentra-:tion of barium ion i.e. the concentration remaining in the intermicellar liquid, will be 0.769 − 0.516 = 0.253 m.e./l.. The degree of interchange is, of course, 516/931 = 0.56.

A similar procedure may be followed in the case of neodymium nitrate. According to Table VII (p. 36) 0.714 m.e./l. of the salt gives the nephelometric value of 694 at 18° C.. This is somewhat less than the value given by 0.667 m.e./l. at 0° C. (Table VI). Thus the concentration has to be increased by rather more than 0.714 − 0.667 = 0.047 to give the same degree of coagulation at 18° C. as at 0° C.. Hence, since the threshold value at 0° C. is 0.500 m.e./l., the value at 18° C. can hardly be more than 0.500 + 0.047 = 0.547 m.e./l.. Assuming that this/

this is actually the threshold value, and that the replacement value is 470 micro-equivalents per litre (i.e., the same as at 0° C.; Table X - page 61), then the equilibrium concentration for the degree of interchange 0.51 will be 0.547 – 0.470 = 0.077 m.e./l. at 18° C..

Further data for 18° C. are contained in Table V (page 34), which gives nephelometric values for the **uncoagulated sulphur** (see page 12), so that **decrease in** the nephelometric value signifies increase in the degree of coagulation. Examination of the figures shows that barium chloride produced complete coagulation between 1.667 and 2.500 m.e./l.. For the purpose of the present argument the "coagulation value" (for complete coagulation) will be taken as 2.500 m.e./l.. Although the true value may be less than this, it cannot be greater.

According to Table XII (page 66), the degree of interchange for complete coagulation by the alkali metals and alkaline earth metals is on the average 0.95. (*) Thus the replacement value will be 0.95 x 931 = 884 micro-equivalents per litre, and the equilibrium concentration of barium ion will be 2.500 – 0.884 = 1.616 m.e./l. at the most.

The/

(*) This is not very different from Weiser and Gray's figures for $BaCl_2$ and $SrCl_2$ (Table XI - p. 65).

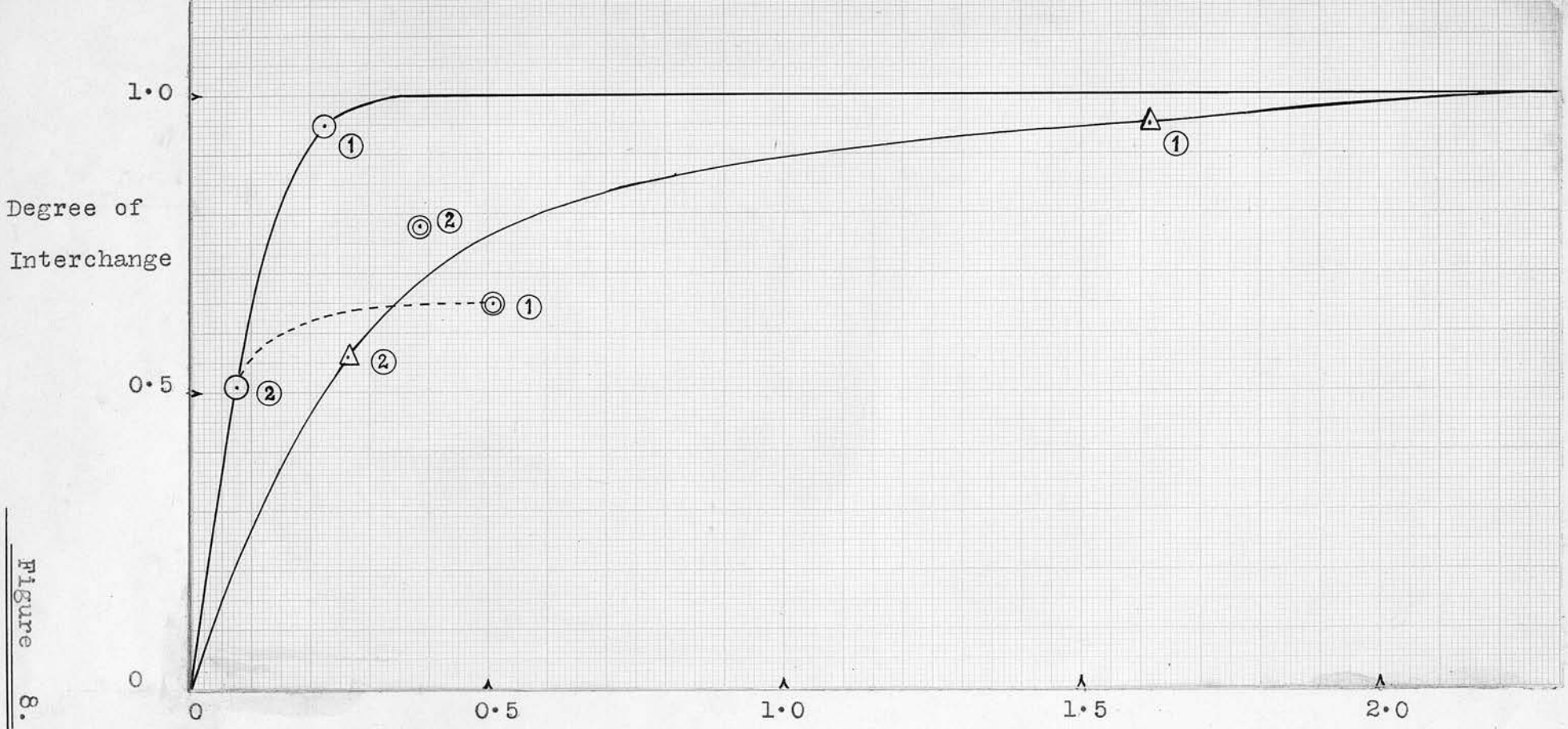

Figure 8.

Salt		Degree of Interchange	Equilibrium concentration of Salt Kation
△ Barium Chloride	①	0·95	1·616
	②	0·56	0·253
⊙ Neodymium Nitrate	①	0·95	0·227
	②	0·51	0·077
◎ Neodymium Nitrate according to Weiser & Gray	①	0·65	0·506
	②	0·78	0·385

The concentration of neodymium nitrate necessary to produce complete coagulation probably lies, for all practical purposes, between 1.111 and 1.250 m.e./l. (Table V - page 34). It certainly cannot be less than 1.111 m.e./l.. Assuming for the present that this is ths actual value and that the degree of interchange is 0.95 (as for barium), it follows that the equilibrium concentration of neodymium ion is 1.111 − 0.884 = 0.227 m.e./l..

The degrees of interchange at 18° C. obtained as above are plotted against the corresponding equilibrium concentrations of salt kation in Figure 8 .

According to Weiser and Gray the degree of interchange for neodymium at the point of complete coagulation is 0.65 (Table XI). This would mean that the replacement value was 0.65 x 931 = 605 micro-equiv./litre, and hence that the equilibrium concentration of neodymium ion was . . . . 1.111 − 0.605 = 0.506 m.e./l.. As will be seen from Figure 8 , it would also mean that for equilibrium concentrations above about 0.350 m.e./l. (intersection of dotted line and barium chloride curve) the replac-
:ing power of neodymium ion is <u>less</u> than that of barium/

barium ion, which is manifestly absurd;

It should be emphasised that the discrepancy is probably greater than appears from Figure 8, since it is almost certain that the actual concentration of barium chloride required to produce complete coagulation was less than the value assumed (2.500 m.e./l.), and that the true coagulation value for neodymium was greater than the assumed value (1.111 m.e./l.). Thus the barium curve* should probably be displaced to the left, and Weiser and Gray's point for neodymium to the right.

Further, it is evident that the neodymium curve obtained on the assumption that the degree of interchange at the point of complete coagulation is 0.95 (i.e., the same as for barium), bears the expected relation to the barium curve, in that they gradually diverge as the concentration increases, up to the coagulation value for neodymium. Moreover, the neodymium curve would according to Weiser and Gray show a sharp inflection long before the interchange is complete. A survey of all available literature revealed no other example of similar behaviour.

Before/

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* i.e., the part above point △②.

Before discussing the possible reasons for the apparent lack of agreement with Weiser and Gray, attention should be called to the following two points. In the first place objection might be raised to the tacit assumption hitherto made, that any effect due to the nature of the salt anion is of negligible proportions. Justification for this view is provided by the observations of Bolam and Muir (loc. cit. page 66(3)) that the relation between interchange and coagulative action is the same for potassium chloride, potassium sulphate, ammonium chloride and ammonium iodide, although the coagulation values show considerable differences. In addition Odén (loc.cit. page 55) found that the coagulation value of the nitrate was practically identical with that of the chloride in the cases examined viz.:- potassium, calcium and barium. Freundlich and Scholz (loc. cit. page 62) also found that the coagulation value of barium chloride was very close to that of barium nitrate.

In the second place it follows from the various considerations advanced that replacement by neodymium will be complete at a concentration of 10 m.e./l. as postulated on page 63 .

Certain features of the work of Weiser and Gray indicate/

indicate that their data hardly warrant the definite conclusions advanced by these workers. The method adopted was to deduce the amount of liberated hydrogen ion from measurement of the potential given by a glass electrode when immersed in the sol + salt mixture itself, not the ultrafiltrate. It was found in the case of the Raffo sol that in the absence of salt the potential corresponded to a hydrogen ion concentration of 850 micro-equivalents per litre.

Weiser and Gray suppose that the hydrogen ions here involved belong to the outer part of the electrical double layer surrounding the particles and " . . .have sufficient osmotic pressure so that they can be measured potentiometrically". Increase in the hydrogen ion concentration due to the presence of added salt is attributed to ionic interchange with the remaining hydrogen ions of the outer layer which " . . . are so firmly held by the $S_x O_6^{--}$ layer that they do not influence the hydrogen electrode".

Thus only the <u>increase</u> on 850 micro-equiv. per litre is reckoned as due to interchange. Hence since the concentration of hydrogen ion reaches a maximum value of 1860 at sufficiently high salt concentrations, the maximum replacement is taken as being

1860 − 850 = 1010 micro-equiv. per litre.

It/

It is obvious, however, that if the 850 micro-equiv. does belong to the outer layer, then it must also undergo interchange, so that the maximum replacement should be 1860 micro-equiv.. On the other hand,it is probable that some of the hydrogen ion in the pure sol was due to acid present in the intermicellar liquid. Thus Bassett and Durrant[1] have shown that there is a definite equilibrium between the polythionic acid adsorbed on the particles and a certain proportion situated in the interior of the liquid surrounding them. Moreover Bolam and co-workers[2] found that the ultrafiltrates from sols dialysed for periods comparable to that employed by Weiser and Gray, invariably contained acid, the lowest concentration observed being 240 micro-equiv. per litre.[3]

In view of these considerations, Weiser and Gray's data for neodymium nitrate (Raffo sol) take on a somewhat different aspect. It is stated that complete coagulation is produced by 1.323 m.e./l. of this salt, when the total hydrogen ion concentration is 1.510 m.e./l.. Obviously the replacement value cannot/

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(1) Bassett and Durrant, loc. cit. page 59.

(2) Bolam, Bowden and Muir, loc. cit. page 66.

(3) bolam and Muir, loc. cit. page 66, Sol J'.

cannot be greater than 1323 micro-equiv., but there is reason to believe that it will not be much less. According to the data in the present investigation (Table X - page 61) the replacement value for 0.500 m.e./l., neodymium nitrate is 470 micro-equiv., so that 96% of the neodymium ion is taken up by the particles. Moreover in two direct determinations of the "adsorption" of neodymium ion, ① Weiser and Gray found that 3480 of 3680 micro-equiv. of Nd^{+++} (i.e., 94%) were taken up in one case, and 1260 of 1340 (i.e., 94%) in the other. ② Thus it is justifiable to assume that the replacement value for 1.323 m.e./l. (see above) was 1323 x 0.94 = 1244 micro-equiv.. Further it may reasonably be supposed that the difference of 266 micro-equiv. between the total hydrogen ion concentration (1510 micro-equiv.) and the replacement value (1244 micro-equiv.) was the amount of intermicellar acid in the pure sol. From this it follows that the maximum interchange was 1860 − 266 = 1594, and that the degree of interchange at the coagulation point was $^{1244}/_{1594}$ = 0.78. This is notably higher than the value (0.65, Table XI - page 65) according/

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① These determinations were made with Raffo sols other than that employed for the hydrogen ion measurements.

② Table I on page 1164 of Weiser and Gray's paper.

according to Weiser and Gray's reckoning, and would account for part at least of the apparent discrepancy between the results of these workers and those of the present investigation. ①

Examination of Weiser and Gray's figures also reveals a good deal of apparent inconsistency. According to their direct determinations of the amounts of kation taken up by the particles at the coagulation point ② we have the following ratios:-

Nd^{+++} : Ba^{++} = 0.68 : 0.73 = 0.93 for one sol, and

Nd^{+++} : Ba^{++} = 0.74 : 0.52 = 0.70 for the other.

Thus the interchange appears to be practically complete in one case, and very much lower in the other.

Weiser and Gray's results are also anomalous in that their curve for the liberation of hydrogen ion (Raffo sol) by barium chloride lies <u>above</u> the neodymium nitrate curve up to the coagulation value of the latter salt, the two curves practically coinciding at higher concentrations. In view of the evidence that neodymium is the more strongly replacing/

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① Note that if 0.78 is taken as the degree of interchange an anomalous curve is still obtained in Figure 8. See point ⓞ ②.

② Table I on page 1164 of Weiser abd Gray's paper.

replacing ion, some error must be involved here.

It is well known that under certain conditions, salts with polyvalent metallic ions reverse the charge on originally negative particles. The phenomenon has been much studied, but opinions still differ with regard to its cause.① On the whole the evidence suggests that it is due to the action of hydrolytic products of the salt. Assuming this to be the case, it would seem that these products must have a destabilising action on a negative sol when present at concentrations insufficient to cause reversal of charge and stabilisation. Since the sols employed by Weiser and Gray were much less acid than the one used in this investigation, it might be suggested that in the case of the former, coagulation by the polyvalent metallic ions was due partly to hydrolysis of the respective salts. It is difficult, however, to gauge the extent of this effect, if operative. Moreover it is hardly consonant with the fact that the degrees of interchange for neodymium and thorium salts are quite close (Table XI - page 65), although the salts differ greatly in the extent to which/

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① Thomas "Colloid Chemistry" (1934) 190 - 193; Breese and Lewis, Trans. Faraday Soc., 34 (1938) 787; Pennycuick, Z. phys. Ch., 148 (1930) 411; Kermack and Voge, Proc. Royal Soc. Edin., 45 (1924-5) 90; Pauli and Fuchs, Koll. Beih., 21 (1925) 412.

which they hydrolyse under comparable conditions.

Verwey ① states that "The exchange may accompany the flocculation but is not essential for it", and that "the exchange is not important for a general flocculation theory". Kruyt ② holds the same views, which are based on an investigation by Verwey and Kruyt ③ on the interchange in silver iodide sols. To quote a recent statement by Verwey ④ in this connection, "In the case of AgI sol . . . . it was shown that the ionic exchange, even of polyvalent ions (UO_2^{++} , Pb^{++} , Ce^{+++}) has nothing to do with the flocculation phenomenon, and from our considerations . . . . . it will be clear that this must be the general case".

According to Verwey and Kruyt, their results show that the coagulating concentration of salt may be less than, equal to, or greater than the concen-:tration required to displace completely the hydrogen ions from the outer part of the double layer, in these particular silver iodide sols. It is therefore concluded/

① Verwey, Chem. Reviews., 16 (1935) 363 (see page 407).

② Symposium on "Hydrophobic Colloids" (see page 7 of thesis), Kruyt, page 13.

③ Verwey and Kruyt, Zeitschr. phys. Ch., 167 A (1933) 312.

④ Reference ② above, Verwey, page 77.

concluded that the degree of interchange at the coagulation point is not necessarily the same for all salts. Stress is laid on certain instances in which it appeared that a much higher concentration of salt was required to produce complete coagulation than to effect complete replacement. It is obvious that if this state of affairs can exist, then the interchange is at least not sufficient to cause coagulation.

Two recent investigations of silver iodide sols suggest that in some cases at least, Verwey and Kruyt's interpretation of their observations is open to question. Weiser, Milligan and Coppoc ① find that the sols are polydisperse and hence undergo fractional coagulation. For example about 98% of the disperse phase in one of their sols was coagulated by 1.2 m.e./l. barium chloride, whereas the finest particles were not coagulated until over 2.4 m.e./l. of the salt was present. It follows that the interchange might <u>appear</u> to be complete at the lower concentration, since the small increment due to the finer particles might well be obscured by the usual experimental error in the determination of the degree of/

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① Weiser, Milligan and Coppoc, J. Phys. Ch., <u>42</u> (1938) 427.

of interchange.

The other investigation, due to de Bruyn and Overbeek[1] (working in Kruyt's laboratory), is concerned with the purity of the sols. It is shown that in general sols prepared by the method of Verwey and Kruyt do not contain, as was assumed by these workers, hydrogen ions alone as counter ions. The outer layer of the particle contains a proportion of other ions derived from the large volume of water used in dialysing the sols. In one instance the outer layer was made up as follows: 50% H^+, 7.5% Cu^{++}, 10% Zn^{++}, and 32.5% of other ions (perhaps K^+ and/or Ca^{++}). Moreover, de Bruyn and Overbeek remark that in a number of sols examined, the content of foreign ions varied from 1/3 to twice that of hydrogen ion. It is clear that the replacement of hydrogen ion might in these cases be practically complete before the whole of the counter ions were displaced by the coagulating kations, so that the ionic interchange would appear complete at a concen-
:tration of coagulant less than the actual concentra-
:tion required.

There are direct indications that these consid-
:erations/

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[1] de Bruyn and Overbeek, Koll. Zeitschr., 84 (1938) 186.

:erations apply, at least to some extent, to the data of Verwey and Kruyt. It was found ② that while the outer layer in sol XV consisted entirely of hydrogen ions, that in sol XIII contained a small amount of ammonium ions, and that in sol XVIII about 20% of ions (unidentified) other than hydrogen. While the data are not sufficient to make a definite statement in the case of the other sols investigated, it obviously cannot be assumed that their outer layers invariably contained hydrogen ions alone.

That Weiser, Milligan and Coppoc's suggestion with regard to fractional coagulation may also apply, is indicated by the data for the coagulation of sol XIII by cerium nitrate. ① According to Verwey and Kruyt, a concentration between 0.64 and 0.74 m.e./l. of this salt was required to produce complete coagulation, but only 0.475 m.e./l., to produce complete replacement. However, it is also recorded that <u>partial</u> coagulation occurred at 0.475 and 0.64 m.e./l.. In the absence of information with regard to the extent of this partial coagulation, it is permissible to assume that coagulation was almost complete/

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① Pages 320 and 321 of Verwey and Kruyt's paper. Note that the composition of the outer layer was known in this case.

② Pages 320 and 322 of Verwey and Kruyt's paper.

complete at 0.475 m.e./l., so that only a small amount of finely dispersed colloid remained to be coagulated at the higher concentrations. The replacement of hydrogen ion from this small fraction of colloid might well be too small to detect, so that replacement would appear to be complete at the lower concentration, though not so in reality.

In view of the considerations advanced in the foregoing, it is justifiable to regard the data of Weiser and Gray, and of Verwey and Kruyt, as at least ambigious. On the other hand, the results of the present investigation are consistent with those obtained in the previous work of which this is an extension, and augments the evidence that in these sulphur sols the degree of interchange is the same for the various salts when comparison is made at concentrations which produce the same degree of instability. This constancy is the more striking when the equilibrium concentrations of the salt kations are compared. For example, the data in Table X (page 61) show that the degree of interchange is constant to within a few per cent, although the equilibrium concentration of the lithium ion (150 m.e./l.) is 5000 times that of the neodymium ion/

ion (0.500 − 0.470 = 0.030 m.e./l.), and about 1000 times that of the barium ion (0.673 − 0.516 = 0.157 m.e./l.). It is evident that the interchange must play an important part in the coagulation process.

The position may be summed up as follows. Any comprehensive theory of the mechanism of coagulation must take into account the following facts regarding the behaviour of sulphur sols stabilised by polythionic acid. (1) the concentration of salt required to coagulate a given fraction of the sol may be identical with or less than, but is never greater than the concentration required to replace completely the hydrogen counter ions from the sulphur micelles constituting that fraction. (2) the greater the concentration of acid in the intermicellar liquid of the sol, the smaller the proportion of hydrogen ion replaced at the coagulation point[1]. (3) the degree of interchange at the coagulation point is the same for all salts. Thus if we consider the simplest case, viz., that of a mono-disperse sol containing the minimum amount of intermicellar acid, it appears that the necessary and/

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① Bolam and Muir (loc. cit. p. 66) found that the replacement was complete with well dialysed sols.

and sufficient condition for coagulation is the complete substitution of the hydrogen counter ions by the kations of the coagulant.

Complete substitution of the hydrogen ion means, of course, that the salt kations are so disposed in relation to the polythionate anions on the surface of the particle that the hydrogen ions cannot displace them. Obviously the simplest explanation of this state of affairs is that the salt kations form undissociated molecules or associated ion - pairs (Bjerrum) ① or some other kind of electrically neutral complexes with these polythionate ions. In other words the diffuse outer layer or atmosphere of counter ions disappears, and the surface of the particle becomes electrically neutral, i.e.,is actually discharged. On this view Freundlich's theory is in principle valid.

Weiser believes that the coagulation is produced by the salt kations which take part in the interchange. He, however, assumes that the particles are not discharged but that the replacing ions are situated nearer to the surface than were the original counter ions/

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① See McBain & Peaker, Proc. Royal Soc., A 125 (1929) 394.

ions. The consequent decrease in the thickness of the double layer is assumed to determine the hypothet-:ical electrokinetic potential, and hence, in some quite unspecified manner, to decrease the stability of the sol. The alleged inequality in the degrees of interchange by neodymium and barium salts at the coagulation point arises because the neodymium ions approach more closely to the surface than the barium ions and hence less of them need enter the double layer to produce the requisite decrease in thickness. Since the closer the kations tend to approach the surface, the more strongly do they displace the hydrogen ions, it follows that "The displacement of hydrogen by kations at the precipitation value approaches equivalence only in case the respective precipitation values are relatively close together".①

It appears, however, that even if Weiser and Gray's results for sulphur sol are accepted as they stand, they do not warrant this conclusion. According to these results, lithium, sodium, potassium and calcium have smaller replacing powers than barium.② It follows from Weiser's arguement, therefore, that replacement at the coagulation point cannot be less for lithium etc. than for barium. Hence since replacement/

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① page 1174 of Weiser and Gray's paper, loc. cit. p. 64 .

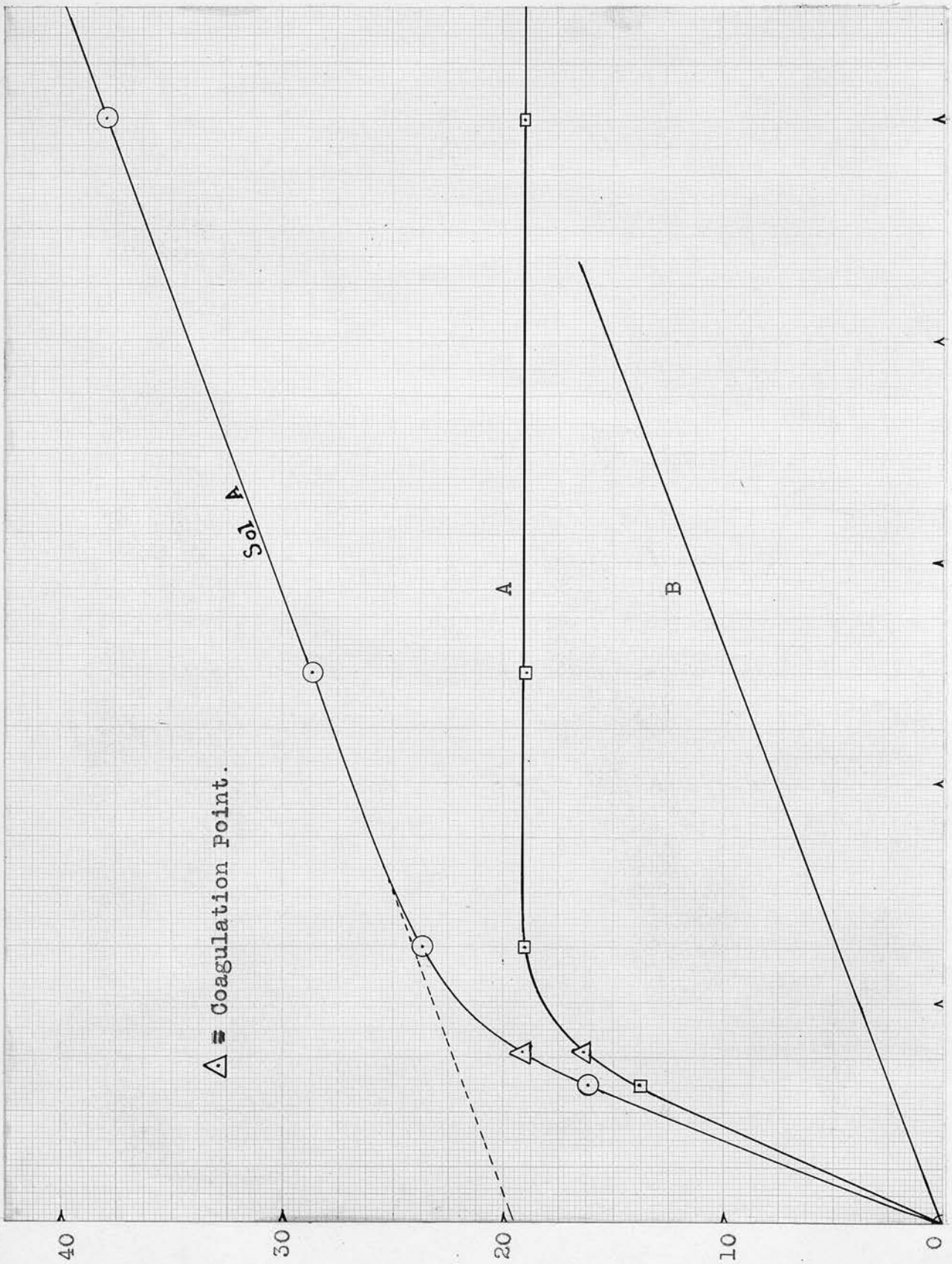
② This is the general rule.

replacement by barium is complete, it must also be complete in the other cases. Thus the degree of interchange is the same for all these ions, although the coagulation concentration of barium differs from the coagulation concentrations of lithium etc. by as much or more than it differs from that of neodymium, aluminium, and thorium. Strictly speaking, of course, the equilibrium concentrations should be compared, and when this is done, the inapplicability to their own data of the above quoted statement of Weiser and Gray becomes even more evident.

Stearic Acid.

As will be gathered from Table XIV (page 52). a freshly prepared stearic acid sol showed no acidification of the intermicellar liquid on addition of a neutral salt. According to previous work (1) such acidification is due to interchange between the salt kations and hydrogen ions furnished by the stearic acid molecules in the surface of the particles. It is therefore tentatively suggested that the above "ageing" effect may be due to re-orientation of the surface molecules so that the carboxyl group is brought into contact with the aqueous phase. The effect has not/

(1) Achar and Usher, J. C. S., 1927. 1875.
Bolam and Duncan, J. C. S., 1936, 1317.



Influence of Salt Concentration on Replacement Value.

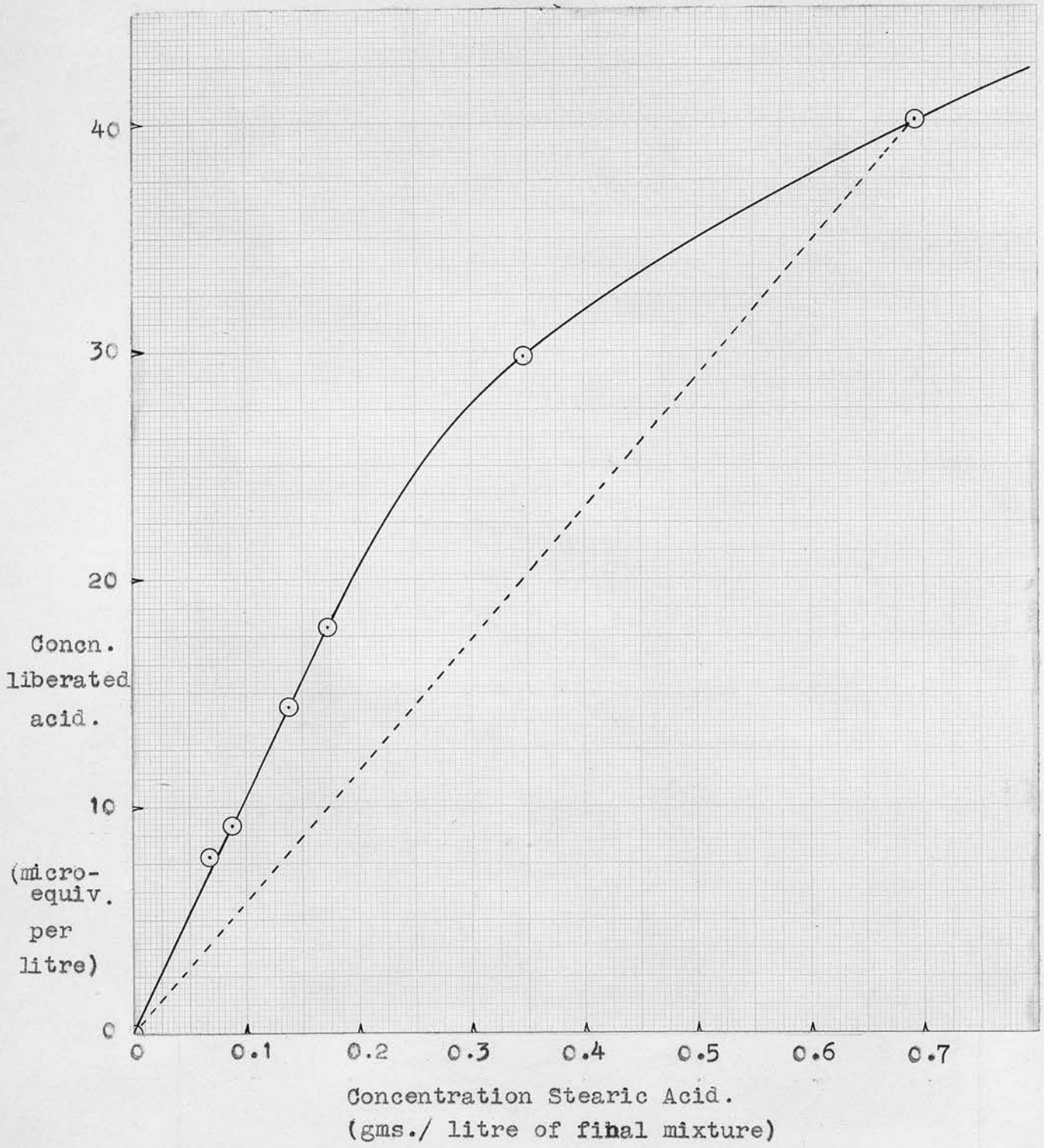
Figure 10.

not been observed before and was quite unexpected.

Equlibrium was established in about 24 hours and the graphs presented in Figures 10 and 11 apply to sols all several days old. The curve in Figure 10 (see Table XV - page 52) shows the manner in which the amount of interchange varies with the concentration of salt. It is different in type from the curves obtained with other systems which have been studied, e.g., sulphur, copper ferrocyanide, and silver iodide. In these cases the interchange increases in a regular manner with increase in the salt concentration up to a maximum, the curve thereafter, of course, running parallel to the concentration axis (see Figure 8 - page 71). On the other hand in the case of stearic acid while the curve shows a marked inflection in the neighbourhood of the coagulation point, the inter-:change continues to increase, in linear fashion, with increase in the salt concentration. Similar curves for stearic acid were obtained by Achar and Usher, and Bolam and Duncan (loc. cit. page 88).

It will be seen that the curve in Figure 10 may be represented as the combination of the other two curves in the same figure. In other words it would appear that the interchange is of two types, the one (A) giving the normal curve, while in the case of the other (B) the amount of interchange is directly proportional to the salt concentration.

The/



Influence of Sol concentration on Replacement Value.

Figure 11.

The graph in Figure 11 shows the manner in which the interchange varies with change in the concentration of the sol, the concentration of the salt being kept constant. It is evident that the departure from a linear relationship (as indicated by the dotted line) means that the amount of hydrogen ion liberated per unit mass of stearic acid increases on diluting the sol. This appears to be the normal behaviour of stearic acid sols, since it was also observed by Achar and Usher, and Bolam and Duncan (loc. cit.). According to these workers the effect is due to increase in the degree of ionisation of the stearic acid molecules in the surface of the particles as the number of particles per unit volume of sol decrease:es. Actual calculation in the case of sol C shows that for concentrations of stearic acid less than about 0.200 gms./litre, the replacement has a constant value of about 105 milliequivalents hydrogen ion per gram stearic acid, which therefore represents the total amount of ionisable surface molecules, i.e., of molecules orientated with the carboxyl group in contact with the aqueous phase.

Reverting to the graph for sol A in Figure 10, it is tentatively suggested that the intercept of the/

the extension of the linear part (dotted line) gives the amount of surface molecules actually ionised at the given concentration of stearic acid, which is $1.215/_2$ = 0.615 gm./litre. On this view the ionised surface acid amounts to $19.5/_{0.615}$ = 31 micro equivalents per gram stearic acid. The maximum amount of ionisable acid will be 105 x $1.215/_{1.385}$ = 92 microequivalents per litre, assuming that sols A and C are strictly comparable in this respect. It follows that about one in every three of the available surface molecules is ionised. This appears to be an improbably high degree of ionisation for a long chain fatty acid, but it must be borne in mind that the ionisable molecules may be so situated that they do not influence each other to the same extent as in a close packed monolayer where, according to McBain and others (1), about one in seven molecules are ionised.

Taking the above point of view it appears to follow that curve (A) in Figure 10 represents inter-:change of the normal type, i.e., between hydrogen counter ions and the salt kations, while curve (B) represents some type of interaction with the unionised stearic/

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(1) McBain & Peaker, Proc. Royal Soc., A 125 (1929) 394;
McBain & Dubois, Z. Elektrochem., 37 (1931) 651;
Dubois & Roberts, J. Phys. Chem., 35 (1931) 3070.

stearic acid molecules. Evidently only the former type of interchange is involved in the coagulation, and it will be seen from Table XVI and Figure 10, that this is completed just above the coagulation point. That this type of interchange is not complete at the coagulation point may be ascribed to the presence of a considerable proportion of amicronic particles which would require a higher concentration of salt to effect complete replacement than the coarser particles whose coagulation point was deter-:mined by the method here employed (see page 49). That stearic acid sols are polydisperse and contain amicrons has been demonstrated by Bolam and Duncan (loc. cit.).

It may therefore be concluded that coagulation of a given fraction of the particles in a stearic acid sol takes place when the interchange is complete for that fraction, and hence that coagulation is due to discharge of the particles by the formation of electrically neutral complexes between the stabilising stearate ions and the salt kations, as in the case of sulphur sols.

SUMMARY.

(1) The action of salts in liberating hydrogen ions, by ionic interchange, from the micelles in (Raffo) sulphur and stearic acid sols has been investigated with regard to the coagulating action of the salts.

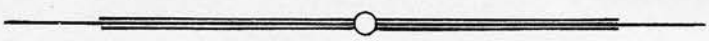
(2) The data support the view that in the case of sulphur sols, the amount of interchange which accompanies the coagulation of a given fraction of the colloid is the same for all salts with monovalent, divalent, and (in the absence of hydrolysis) trivalent metallic kations.

(3) The data for the stearic acid sols indicate that in the case of these systems two types of interchange are to be distinguished, one of which is involved in the coagulation of the colloid by salts.

(4) It has been observed that stearic acid sols "age" in respect to stability and degree of ionic interchange.

(5) The importance of the study of ionic interchange for a general theory of coagulation is discussed. It is concluded that the results of the/

the present investigation are consistent with the view that in sols stabilised by adsorbed ions or ions originating from the dissociation of surface molecules, the formation of electrically neutral complexes with the coagulating kations is an essential condition for coagulation.



In conclusion the author wishes to express his thanks to Dr. T. R. Bolam for his assistance during the course of this investigation. Also his grateful thanks to the 'Earl of Moray Endowment Fund' for a grant towards the purchase of apparatus.